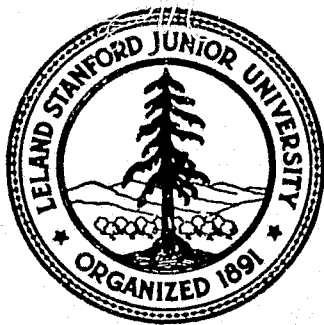


## **General Disclaimer**

### **One or more of the Following Statements may affect this Document**

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.



CMR-76-8

(NASA-CR-148579) MATERIALS RESEARCH AT  
STANFORD UNIVERSITY Annual Report, 1 Jul.  
1975 - 30 Jun. 1976 (Stanford Univ.) 411 p  
HC \$11.00 CSCL 05A

N76-30026

Unclas  
48173

G3/70

Fifteenth Annual Report

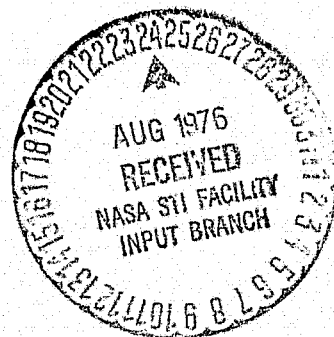
on

MATERIALS RESEARCH

AT

STANFORD UNIVERSITY

July 1, 1975 - June 30, 1976



CENTER FOR MATERIALS RESEARCH

STANFORD UNIVERSITY • STANFORD, CALIFORNIA



Fifteenth Annual Report

on

MATERIALS RESEARCH AT STANFORD UNIVERSITY

Information concerning research activities related to the science of materials during the period July 1, 1975 through June 30, 1976.

This research was supported primarily by one or more of the following agencies of the United States Government:

Defense Advanced Research Projects Agency  
Department of the Air Force  
Department of the Army  
Department of Commerce  
Department of Health, Education and Welfare  
Department of the Interior  
Department of the Navy  
Energy Research and Development Agency  
National Aeronautics and Space Administration  
National Bureau of Standards  
National Science Foundation  
Veterans Administration

July 1976

Reproduction in whole or in part is permitted for any purpose of the United States Government.

THE CENTER FOR MATERIALS RESEARCH  
STANFORD UNIVERSITY  
STANFORD, CALIFORNIA

Director - Robert A. Huggins

Executive Committee

David M. Barnett, Materials Science and Engineering; Mechanical Engineering.

James P. Collman, Chemistry

Theodore H. Geballe, Applied Physics; Materials Science and Engineering

Robert A. Huggins (Chairman), Materials Science and Engineering

William A. Little, Physics

Gerald L. Pearson, Electrical Engineering

William E. Spicer, Electrical Engineering; Materials Science and Engineering

David A. Stevenson, Materials Science and Engineering

Assistant Director - Frank E. Gallagher

Laboratory Director - Troy W. Barbee, Jr.

Administration - Malinda B. Larry

Accounting - Elizabeth T. Winfield

Room 105 McCullough Building  
Stanford, California 94305  
(415)497-4118

## TABLE OF CONTENTS

	Page
A. INTRODUCTION	1
B. MATERIALS RESEARCH PROGRAMS	3
1. Elastic and Thermal Properties of Composite Materials, A. Acrivos	3
2. Chemical Metallurgy, R. N. Anderson	5
3. Acoustic Waves and Devices, B. A. Auld	10
4. Synthesis of Non-Equilibrium Microstructures by Vapor Deposition, T. W. Barbee, Jr.	14
5. Continuum Theory of Lattice Defects, Fracture, and Surface Waves in Anisotropic Elastic Media, D. M. Barnett	25
6. Photoelectronic Materials Physics, C. W. Bates, Jr.	29
7. Electromagnetic Properties of Superconductors, M. R. Beasley	38
8. Structures of Amorphous Materials, A. I. Bienenstock	41
9. Properties of Adsorbents and Catalysts, M. Boudart	45
10. Intrinsic Chemical Reactivity, J. I. Brauman	49
11. Crystal Chemical Studies of Crystalline and Amorphous Silicates, G. E. Brown	53
12. Photoelectronic Properties of Solids, R. H. Bube	60
13. X-Ray Excitation of Superatmospheric Lasers, R. L. Byer	69
14. Studies in Homogeneous Catalysis and the Synthesis of Metal-Metal Bonds, J. P. Collman	72
15. Interactions of Solids with Solutions, F. W. Dickson	77
16. Methods of Quantum Field Theory Applied to Cooperative Phenomena Problems, S. Doniach	80
17. Coal Slag Phenomena in Open Cycle MHD Generators, R. H. Eustis	84

18.	Experiments at Liquid Helium Temperatures on Macroscopic Quantum Effects, Material Properties, General Relativity, and Superconducting Accelerators, W. M. Fairbank, C. W. F. Everitt, R. P. Giffard and H. A. Schwettman	86
19.	Excited State Dynamics and Energy Transport in Molecular Solids, M. D. Fayer	99
20.	Crystal Growth Research, R. S. Feigelson	105
21.	Macromolecular Research, P. J. Flory	113
22.	Metal Fatigue, H. O. Fuchs	117
23.	Superconducting Power Transmission Line Materials Research, T. H. Geballe and M. R. Beasley	119
24.	Low Temperature Properties of Materials, T. H. Geballe	122
25.	Ion Implantation in Semiconductors and Proton-Enhanced Diffusion, J. F. Gibbons	126
26.	Mössbauer Effect and Related Phenomena, S. S. Hanna and B. B. Triplett	132
27.	Generation of Ultraviolet and Vacuum Ultraviolet Radiation, S. E. Harris and J. F. Young	150
28.	Pseudopotential Methods in Physics, W. A. Harrison	153
29.	Dynamic Dark-Field Electron Microscopy, G. B. Haydon	155
30.	Fracture of Compact Bone, W. C. Hayes	158
31.	Mechanical Behavior of Composites Under Impact, G. Herrmann	161
32.	Structural Studies of Proteins, K. O. Hodgson	164
33.	Physical Studies of Molecules of Biological Interest, B. S. Hudson	170
34.	Solid State Electrochemistry, R. A. Huggins	177
35.	Acoustic Interactions with Solids, G. S. Kino	181
36.	Analysis of Metal-forming, Impact, Wave Propagation in Heterogeneous Media and Formulation of Constitutive Relations, E. H. Lee	186

37.	Structure of Dense Fluids, J. E. Lind, Jr.	190
38.	Superconductivity and Molecular Physics, W. A. Little	194
39.	Experimental and Theoretical Studies on Rock-Forming Systems at High Temperatures and Pressures, W. C. Luth	196
40.	Reactivity of Solids, R. J. Madix	198
41.	Electrocatalytic Studies Employing Solid-State Oxide Electrolytes, D. M. Mason	203
42.	Epitaxial Crystal Growth, B. L. Mattes	205
43.	Physical Chemistry of Lipid, Lipid-Protein or Lipid-Detergent Bilayer Membranes, H. M. McConnell	309
44.	Integrated Electronics, J. D. Meindl	215
45.	Relations Between Crystalline Imperfections and the Physical Properties of Crystals, W. D. Nix	219
46.	Recrystallization of Quartz Under Non-Hydrostatic Stress, A. M. Nur	228
47.	Time Dependent Crustal Deformation, A. M. Nur	230
48.	Velocity and Attenuation of Seismic Waves in Rocks, A. M. Nur	232
49.	Mechanical Processes of Crustal Faulting, A. M. Nur and D. M. Barnett	236
50.	Proton Production from High Energy Electron Beams, R. H. Pantell	238
51.	Physics and Chemistry of Oxides and Oxide Surfaces, G. A. Parks	241
52.	Gas-Liquid Metal Reactions and Interactions. Production of Reactive Metals via Carbothermic Reduction in Solvent Metals. Spent Nuclear Fuel Recovery. Nuclear Waste Utilization and Disposal, N. A. D. Parlee	245
53.	Electrical, Optical and Metallurgical Properties of Semiconducting Material, G. L. Pearson	254
54.	Studies of the Dynamics of Molecules and Macromolecules in Liquids, R. Pecora	260

55. Phase Transition Kinetics, G. M. Pound	263
56. Microwave Electronics, C. F. Quate	272
57. Investigation of the Micromechanics of Expansive Reactions in Concrete, C. W. Richards	274
58. Protein Adsorption to Polymer Films, C. R. Robertson	275
59. Spectroscopy and Quantum Electronics, A. L. Schawlow and T. W. Hänsch	276
60. Interactions of Acoustic Radiation with Solids, H. J. Shaw	282
61. Mechanical Behavior of Solids, O. D. Sherby	288
62. Ultra-Short Optical Pulse Generation and Applications, A. E. Siegman	297
63. Electron Spectroscopy, Surfaces, and Interfaces, W. E. Spicer	303
64. Solid State Physical Chemistry, D. A. Stevenson	323
65. Fundamental Aspects of Reactivity in Inorganic Systems, H. Taube	331
66. Crystallogenics, Surfaces, Stress Corrosion Cracking and Biomaterials, W. A. Tiller	335
67. Biological Physics, M. Weissbluth	340
68. Fundamental Studies of Magnetic Materials. R. L. White	342
C. PUBLICATIONS	346
D. DOCTORAL DISSERTATIONS	367
APPENDICES	
I. FACULTY MEMBERS PARTICIPATING IN MATERIALS RESEARCH	372
II. RESEARCH ASSOCIATES AND PROFESSIONAL STAFF	375
III. GRADUATE STUDENTS PARTICIPATING IN MATERIALS RESEARCH PROGRAMS	379
IV. GRADUATE DEGREES CONFERRED	383
V. NAME INDEX	387

## SECTION A

### INTRODUCTION

This Fifteenth Annual Report includes information briefly describing the total research activity related to the science of materials at Stanford University during the period July 1, 1975 through June 30, 1976.

This report contains brief descriptions of the various individual research programs active during this period. The organization of such a large and varied compilation presents a serious problem. Many programs are cooperative and involve several faculty members, and there are many faculty members with catholic interests, so that arrangement by subject area becomes cumbersome. It was decided that the simplest and most straightforward way to encompass Stanford's broad activities in this area would be an alphabetical arrangement by principal investigator. In addition to brief abstracts relating to the various research programs, compilations are included of publications, doctoral dissertations, faculty and senior staff members, research associates, graduate students and degrees awarded. Finally, a name index has been added for convenience in locating references to the activities of specific individuals. From this compilation, it can be seen that research on materials and related problems is being conducted within eleven different academic departments as well as in the Hansen Laboratories.

The research described herein received financial support from many different sources. As indicated in their descriptions, some of the research programs were supported by private sources. However, most received support from one or more of the following agencies of the United States Government.

Defense Advanced Research Projects Agency  
Department of the Air Force  
Department of the Army  
Department of Commerce  
Department of Health, Education and Welfare  
Department of the Interior  
Department of the Navy  
Energy Research and Development Agency  
National Aeronautics and Space Administration  
National Bureau of Standards  
National Science Foundation  
Veterans Administration

In addition to the direct support of individual research programs by the agencies mentioned above, broad-base core support was furnished by the National Science Foundation through its Materials Research Laboratory (MRL) Program under Grant No. DMR 72-03022 (formerly GH-33630), administered by the Center for Materials Research (CMR), during this past year. Prior to July 1972, this core support was provided by the Advanced Research Projects Agency through its Interdisciplinary Laboratory (IDL) Program.

Besides contributing to the direct support of many individual materials research programs, core funds from this source have been used to help pay the capital costs of some of the laboratory and office space in the McCullough Building. Also of particular importance has been the financial assistance received through these programs for the establishment and operation of a group of vital Central Facilities, which provide a truly unique service to the whole materials research community at the University.



## SECTION B

### MATERIALS RESEARCH PROGRAMS

#### 1. ELASTIC AND THERMAL PROPERTIES OF COMPOSITE MATERIALS

Andreas Acrivos, Professor of Chemical Engineering

##### Graduate Students:

H-S. Chen  
F. A. Gadala-Maria  
T. S. Lo

S. R. Moosman  
R. W. Watkins  
G. K. Youngren\*

\*Received Ph.D. during report period

##### Agency Support:

NSF GK 43608  
NSF ENG-74-23229  
EPRI-RP-314-1

##### Technical Objective:

To develop a theory (substantiated by experiments) for predicting the bulk elastic and thermal properties of composite materials containing dissimilar constituents. Specifically, the aim is to investigate in detail those cases in which the addition of relatively small amounts of a suitably chosen foreign substance can alter substantially parameters such as the effective bulk elastic modulus and the effective thermal conductivity of a simple solid both at steady-state and during the transient regime, as well as to study concentrated composites in which there exists a strong interaction among the individual elements comprising the dispersed phase. The ultimate objective of this work is to provide a rational basis for designing composite materials having desired elastic and thermal properties, e.g., composites having high tensile strength but low weight, or composites which are high conductors of heat in one direction, but act as insulators in the other.

#### Research Report:

##### Elastic Properties of Composite Materials Containing Solid Spheres

Graduate Student: H-S. Chen

A theory has been developed for predicting the effective elastic moduli of composite materials containing small solid spheres in moderate concentrations. Specifically, expressions were derived for the  $O(\phi^2)$  coefficients of the bulk and shear moduli--  $\phi$  being the volume fraction of the spheres--for a wide range of properties of the continuous and discrete phases. These were obtained by applying a technique recently described by Jeffrey for the analogous heat conduction problem. Experiments are being performed to test the theoretical predictions in the more dilute range and to provide much needed data for extending the theory to the concentrated regime.

#### Reference Publications:

1. A. Nir, H. Weinberger and A. Acrivos, "Variational Inequalities for a Body in a Viscous Shearing Flow," J. Fluid Mech. 68, 739 (1975).
2. G. K. Youngren and A. Acrivos, "Stokes Flow Past a Particle of Arbitrary Shape. A Numerical Method of Solution," J. Fluid Mech. 69, 377 (1975).
3. G. K. Youngren and A. Acrivos, "Rotational Friction Coefficients for Ellipsoids and Chemical Molecules with Slip Boundary Condition," J. Chem. Physics 63, 3846 (1975).
4. G. G. Poe and A. Acrivos, "Closed Streamline Flows Past Rotating Single Cylinders and Spheres: Inertia Effects," J. Fluid Mech. 72, 605 (1975).
5. G. G. Poe and A. Acrivos, "Closed Streamline Flows Past Small Rotating Particles: Heat Transfer at High Peclet Numbers," Int. J. Multiphase Flow 2, 365 (1976).
6. H-S. Chen and A. Acrivos, "On the Effective Thermal Conductivity of Dilute Suspensions Containing Highly Conducting Slender Inclusions," Proc. Roy. Soc. London (to appear, 1976).

## 2. CHEMICAL METALLURGY

R. N. Anderson, Associate Professor, Applied Earth Sciences

### Professional Associates:

T. J. Connolly, Professor, Mechanical Engineering  
W. C. Luth, Associate Professor, Geology  
N. A. D. Parlee, Professor, Applied Earth Sciences  
J. D. Khazzoom, Visiting Professor, Operations Research, Stanford

### Consultants:

D. Cubicciotti, SRI, Menlo Park  
C. A. Eckert, University of Illinois, Champaign-Urbana  
K. S. Sree Harsha, San Jose State University

### Graduate Students:

G. E. Beckstead<sup>+</sup>  
T. H. Chin  
B. H. Coyle<sup>\*\*</sup>  
M. Hassan  
H. H. Haung<sup>\*</sup>  
A. Jayarajan  
J. R. Hwang  
W. Y. Lim

\* Received Ph.D. during report period

\*\* Received Engineer's Degree during  
report period.

<sup>+</sup> Received MS during report period.

### Student Assistants:

J. Koperski

### Agency Support

NSF through CMR  
Bureau of Mines GA 133080  
Bureau of Mines GA 133085  
Stanford Institute for Energy Studies

### Technical Objective:

To investigate the thermodynamic, kinetic, and transport phenomena necessary for the development and design of mineral and metallurgical extraction processes.

### Approach:

The approach varies with each study.

## Research Report:

### (1) Recovery of Non-Ferrous Metals from Auto Shredder Refuse

Graduate Student: B. H. Coyle

The objectives of this research program are to develop a hydro-metallurgical method of producing pure zinc, copper and aluminum metals from the nonmagnetic metallic scrap generated by junk automobile shredding operations. An optimum hydrometallurgical circuit has been designed and the economic analysis of a hypothetical 250 ton/day plant have been completed. The chemical kinetics of the hydro-metallurgical operations in the process have been evaluated in the laboratory. The chemical dissolution of zinc alloys in acid has been found to be the rate limiting step in the process. The process is now being improved to recover magnesium metal.

### (2) Pollution-Free Copper Extraction Metallurgy

Graduate Student: H. H. Haung

A mixed lime-concentrate pellet roast process has been developed for the metallurgical treatment of copper sulfide floatation concentrates. Air pollution by  $\text{SO}_2$  is practically eliminated since all sulfur is retained as a solid with the lime. The oxidized copper in the pellet can be dissolved in a sulfuric acid leach and recovered as cathode copper. The critical parameter in this process is the roasting temperature -- temperatures that are too high produce insoluble copper-ferrite and temperatures that are too low produce acid soluble iron sulfate. The various methods by which this extractive metallurgical process can be operated have been investigated including fluidized bed roasting.

### (3) Analysis of an On-Stream Particle Size Analyzer

Graduate Student: T. H. Chin

A model for a new concept of on-stream particle size analysis has been developed and experimentally verified. This analysis method is based on continuously measuring and comparing the percent solids in an internal reference stream containing only undersized particles. A semi-permeable hydraulic system is used so that the mass concentration

in the internal stream can vary and is proportional to the undersize particle mass concentration in the pulp stream. The density changes in the two pulp streams are continuously measured with nuclear gauges.

(4) New Energy Systems for Process Metallurgy

Graduate Student: A. Jayarajan

The enormous energy requirements of the metals industry suggests consideration of new energy alternatives. The MHD generator or high temperature gas turbine seem particularly well suited to the integrated production of metals utilizing electrolytic and carbothermic reduction such as aluminum and steel. In this study, a model of a dedicated MHD facility used in making iron has been investigated. This arrangement is found to be capable of reducing the overall carbon consumption per ton of iron by 1/3. Moreover, metallurgical grade coke is not required in this process. Improved efficiencies are due to the additional MHD energy recovered during the combustion of coal that are normally lost in the conventional iron blast furnace. More detailed modeling of the process is being done to assess the economic impact of utilizing the MHD generator in steelmaking.

(5) Extraction of Germanium and Gallium from Coal Furnace Flue Dust

Graduate Student: M. Hassan

Gallium and Germanium, among other minerals, are found in coal and concentrated in the flue dust upon combustion. Hydrometallurgical recovery by leaching the flue dust to recover these materials is uneconomical. This research program has studied the behavior of these elements during combustion using a knudsen effusion mass spectrometer to identify the vapor species and its characteristics. Based on this study, a high temperature process employing a plasma torch is being designed to alter and extract selected trace minerals in coal flue dust.

(6) The Chemistry and Physical Mechanics of Nuclear Waste in Rocks

Professional Associates: T. J. Connolly  
W. C. Luth

Graduate Student: J. R. Hwang

This study has examined the magma creation in rock systems (basaltic and granitic) as functions of temperature and time. Simulated high level nuclear waste in calcined form have been used to examine the experimental rock-waste interactions occurring. These data are applicable to defining the engineering requirements and safety aspects of high-level radioactive waste disposal in these host rocks. Deep rock disposal appears to be a viable method for the ultimate disposal of high level nuclear waste. The methods of the nuclear waste re-entering the biosphere by magma flow and by leaching of the material have been studied, as well as the behavior of typical container materials suggested for use in this application.

(7) Development of an Energy Analysis Model for the Evaluation of Mineral and Mineral Waste Utilization Processes

Professional Associate: J. D. Khazzoom

Graduate Student: W. L. Lim

It is the object of this study to develop an energy analysis tool specifically tailored for mineral and mineral waste applications. The work will take the form of developing an energy analysis methodology based on sound principals of energy analysis and applying this methodology to appropriate mineral situations such as the recycling of scrap metal.

The planning of effective mineral and mineral waste utilization strategies by government and industry requires comparisons to be made of competing processes and the selection of the optimum path. An effective basis for comparison in the past has been the production costs associated with the various process alternatives. More recently, however, consideration of energy requirements in view of their cost or availability has become equally important in the decision making process. Analysis that incorporates the availability and cost of specific energy sources can be used to identify mineral and mineral waste utilization strategy; to evaluate competing processes; to identify important new research directions; and to recognize potential problems before they occur.

Reference Publications:

"A Technical and Economic Analysis of Processes for the Recovery of Metal in the Non-Ferrous Portion of Automobile Shredder Refuse," Proceedings of the Fifth Annual Mineral Waste Utilization Symposium April 1976.

"Evaluation of Mineral Waste Utilization Processes and Strategies by Net Energy," Proceeding of the Fifth Annual Mineral Waste Utilization Symposium, April 1976.

"MHD Stabilization in the Metals Industry," Presented at the Annual AIME Meeting, Feb. 1976.

"Hydrometallurgical Separation of the Non-Ferrous Portion of Automobile Shredder Refuse," submitted to Conservation and Recycling. Presented Feb. 1976 national AIME meeting.

"Carbothermic Reduction of Refractory Metals," J. of Vac. Sci. & Tech. Vol. 13, No. 1 Jan/Feb 1976. (Presented at American Vacuum Society, Philadelphia, Oct. 1975)

"Beneficiation of Low-Grade Uranium Ores," Presented at the Sept. 1975 American Nuclear Society Annual Meeting and Abstract published in the Transactions.

"The Chemistry and Physical Mechanics of Nuclear Wastes in Rocks," Presented at the Sept. 1975 American Nuclear Society Annual Meeting and Abstract published in the ANS Transaction.

"Thermodynamics of Nitride Formation in Liquid U-Gd-Sn Alloys," J. of High Temp. Sci. 7, 249-258 (1975).

### 3. ACOUSTIC WAVES AND DEVICES

B. A. Auld, Adjunct Professor, Hansen Laboratories

#### Graduate Students:

S. A. Farnow\*  
J. Mein  
J. G. Harris  
D. Pettibone\*\*

\*Received PhD in Physics during  
report period

\*\*Received MS during report period

#### Agency Support:

Navy N00014-75-C-0359  
Navy N00014-75-C-0632  
NSF GK 43143

#### Technical Objective:

To obtain an understanding of acoustic field theory and to apply the basic principles to device development.

#### Research Report:

- (1) Acoustic Fresnel Zone Plates (S. A. Farnow, D. Pettibone and B. A. Auld)

Acoustic zone plate transducers have been constructed to focus sound in water at frequencies near 10 MHz. Photolithographic techniques were used to evaporate gold zone plates (of ten zones) as electrodes on one face of PZT-5A discs, with the opposite face being given a full-face electrode. Focal plane intensity distributions with half widths of 0.22 mm or 1.5 wavelengths have been achieved. An improvement is realized by a poling technique which alternates the polarization of the ceramic in adjacent zones. In this way, the zone plate may be converted to a phase plate, resulting in, among other



improvements, a 4-fold increase in the intensity at the focus.

Acoustic imaging has been performed with these transducers in both transmission and reflection modes. In both cases, the object is mechanically scanned in a water bath in the focal plane of the transducer(s). In the transmission system, the object is insonified from one side with a phase plate transducer. The transmitted sound is then detected from the other side with a second phase plate transducer. A single phase plate transducer is used for reflection imaging, with the system operating in a pulse-echo mode. Resolutions of 1.8 wavelengths have been achieved.

Techniques for electronically scanning the focused beam produced by a phase plate transducer are being investigated. From the operational point of view this is important, since mechanical scanning severely limits the speed with which an image can be recorded. Phased array methods have been devised for producing either a linear scan or a spiral scan of the acoustic beam. Preliminary experiments have been performed on the linear scan system. Two other developments have been the use of double acoustic matching layers on the front face of the transducer, and the conception of a pulse compression type of phase plate. Matching layers broadband the frequency response of the transducer, permitting one to take full advantage of the frequency dependence of the focal length in order to achieve depth scanning. The pulse compression configuration permits one to improve the depth resolution of the system by applying the well-known pulse compression technique of radar systems.

(2) Acoustic Waveguide and Scattering Studies (D. Pettibone, J. Mein and B. A. Auld)

The aims of this program are to analyse the waveguide modes in acoustic systems, to study scattering of acoustic waves at obstacles, to arrive at useful analytic techniques which would be applicable to a large class of problems, and to carry out experimental tests of the theory.

In the course of an investigation by variational methods of the scattering of the fundamental extensional mode at the free edge of semi-infinite isotropic plate, it has been discovered that mechanical reactance functions in acoustic waveguides do not always satisfy Foster's Reactance Theorem. This is a theorem concerning the behavior of lossless electrical circuits where it is of fundamental importance in the theory of electrical filters. The scattering studies we are performing provide a rational basis for designing mechanical waveguide filters, and it is intended to exploit our discovery about the breakdown of Foster's Reactance Theorem in designing such filters. This will involve both field calculations and a search for materials with appropriate mechanical properties.

Another aspect of this program is an investigation of acoustic waveguiding along ferroelectric domain walls. It is well-known that such guided waves exist in the idealized case of a wall in an infinite medium and a simple argument can be made to show that the effect also exists in finite bodies. The choice of material is extremely important here and involves such factors as ease of creating and stability of

domain structures, elastic losses both within and outside of the domain wall, and the possibility of domain wall switching for certain device applications.

#### Reference Publications

- (1) S. A. Farnow and B. A. Auld, "An Acoustic Phase Plate Imaging Device", pp. 259-274, Acoustical Holography Vol. 6 (1975).

#### 4. SYNTHESIS OF NON-EQUILIBRIUM MICROSTRUCTURES BY VAPOR DEPOSITION

T. W. Barbee, Jr., Senior Research Associate, Center for Materials Research

##### Professional Associates:

C. R. Barrett  
M. R. Beasley  
A. I. Bienenstock  
M. Boudart  
T. H. Geballe  
J. F. Gibbons  
R. H. Hammond  
R. E. Howard

G. Ilonca  
D. L. Keith  
C. N. King  
G. M. Pound  
W. E. Spicer  
D. A. Stevenson  
S. Yoshida  
R. B. Zubeck

##### Graduate Students:

A. Gat  
A. B. Hallak  
Z. S. Jan  
G. M. Michal  
D. F. Moore

R. H. Norton  
J. R. Salem  
R. A. Thomas  
N.-H. Tsai

##### Sources of Support:

NSF/MRL Thrust Program on Alloy Catalytic Materials  
NSF/MRL Thrust Program on Synthesis, Characterization and  
Properties of Noncrystalline Metallic Alloys  
NSF/RANN AER72-03572 under Professors Beasley and Geballe

##### Technical Objective:

Development of new materials by control of microstructure through use of the vapor deposition process in a manner insuring that process parameters, rather than thermally activated bulk mechanisms, are controlling the resulting microstructure.

##### Approach:

An experimental study of the vapor deposition process, particularly as it applies to the synthesis of non-equilibrium structures, has been the general approach taken in this program. Particular emphasis has been placed on synthesis of extremely fine powders by gas phase reactions occurring under strongly non-equilibrium conditions, synthesis of glassy

or amorphous metals by vapor quenching, and deposition of intimate mixtures of materials having controlled microstructures.

Research Report:

(1) Superconducting Power Transmission Line

Professional Associates: M. R. Beasley, T. H. Geballe,  
R. H. Hammond, R. E. Howard,  
D. L. Keith, C. N. King, R. B. Zubeck

Graduate Students: A. B. Hallak, D. F. Moore, R. H. Norton  
J. R. Salem, R. A. Thomas

This work, carried on in the Vapor Phase Synthesis Facility of the Center for Materials Research, has been undertaken in cooperation with and in support of the Superconducting Power Transmission Line Program under the direction of Professors T. H. Geballe and M. R. Beasley. The work in the Central Facilities has emphasized exploration of methods for controlling the microstructures of superconducting layers deposited by dual electron beam evaporation techniques so that optimum properties for application to superconducting power transmission lines might be obtained.

Over the past year, emphasis has been on multilayer composites of  $\text{Nb}_3\text{Sn}$  and normal metal (pinning) barriers. Such structures are of interest in that there are theoretical bases for expecting enhanced properties pertinent to superconducting power transmission line applications. In general, the properties of interest are critical current, AC losses and line stability.

A systematic investigation carried on primarily by the participants in the program using equipment available in CMR's Central Facilities has demonstrated that good surfaces and growth morphologies can be obtained under optimum deposition conditions in single layers. Further, multi-layered structures such as are desired for superconducting power transmission line applications have been synthesized with acceptable surface character. The observed behavior as affected by different deposition conditions can be largely rationalized on the basis of several recent fundamental studies on the surface and growth morphologies of vacuum deposited thick and thin films. These studies have occurred both at Stanford and in other laboratories and provide a firmer scientific base for the synthesis efforts in this program.

Reference Publication:

1. R. B. Zubeck, C. N. King, D. F. Moore, T. W. Barbee, A. B. Hallak, A. Salem and R. H. Hammond, "Growth Morphologies of Thick Films of  $\text{Nb}_3\text{Sn}$  Formed by Electron Beam Evaporation", presented at Int. Conf. of Metallurgical Coating, San Francisco (April 1976).

(2) Synthesis of Fine Particles for Catalytic Activity Studies

Part of Thrust on Alloy Catalytic Materials

Professional Associates: M. Boudart, D. L. Keith,  
W. E. Spicer, S. Yoshida

By necessity, catalytic materials must exhibit surface areas in the  $100 \text{ m}^2 \text{ g}^{-1}$  range, corresponding to particle sizes in the vicinity of 10 nm. No one had reported the preparation of WC particles in this size range until our recent work at Stanford actually achieved their synthesis in the Central Facilities of the Center for Materials Research. The effectiveness of fine particle synthesis by vapor condensation in reactive gases has been demonstrated in a series of experiments in which a range of compounds including tungsten carbide have been produced.

Carbides of refractory elements are commonly prepared by powder metallurgy. In general, direct reaction of the metal or metal-halide with carbon is the most common technique. As will be discussed in the following the reaction used to synthesize tungsten-carbon compounds in this thrust research program is a strongly non-equilibrium adaptation of one of the known methods.

Initial work here revolved about the "smoke" formation originally reported by Pfund and more recently extended by a number of Japanese investigators for elemental materials. In general, this process consists of evaporating a metal into a poor vacuum ( $P > 1$  Torr inert gas) where the mean free path is less than  $10^{-3}$  cm. It leads to a nucleation and growth sequence directly analogous to those described by the classical theories of nucleation and growth from the vapor of either liquid droplets (early in the process) or crystalline solids (later in the process). This approach can be adapted for synthesis of compounds, carbides and nitrides in particular, by including a reaction component ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{NH}_3$ ) in the gas atmosphere. This has been done in CMR's Central

Facilities. Carbides and nitrides of vanadium, zirconium, titanium and carbides of iron in particle sizes from 4 to 200 nm have been prepared. This development provided the basis for the approach to the synthesis of compounds of tungsten and carbon.

It was immediately apparent that the source of metal atoms (tungsten) would be a major problem. The melting points of the materials studied (Fe, V, Ti, Zr) had a maximum of approximately 2200 K, whereas the melting point of tungsten is approximately 3700 K. In order to avoid this problem an alternate approach was used: A volatile compound of tungsten was used as the metal atom source. Possible compounds included  $WCl_6$  and  $WO_3$ , due to their high vapor pressures at low temperatures, and  $WCl_6$  because of its easy dissociation. Each of these have been studied as W atom sources and  $WCl_6$  has been found to be most effective.

The experimental arrangement used in the synthesis to date is a batch system in which a volatile halide of the metal is reacted over a hot filament with a reactive gas to form the desired compound. The reaction zone is thermally inhomogeneous with large temperature gradients about the heated filament.

A resistance heated baffle box vapor source is used in an enclosure held at pressures varying from 10 to 100 Torr. The tungsten atom source compound is loaded through access A which is subsequently plugged. The source is contained in a tight enclosure and the system evacuated and purged with pure argon twice to provide a nonoxidizing atmosphere prior to backfilling with the reactive atmosphere. Emphasis is placed on the control, of course, of temperature, typically between 600 and 900 K. The tungsten filament is held at 1600 K and the vapor passed over it where it reacts with the containing atmosphere from 1300 to 1900 K. Typical reacting gases are isobutanol, acetylene, and methane mixed with hydrogen and in some experiments, an inert gas. Reaction products are highly divided materials consisting of  $\beta WC_{1-x}$ ,  $\alpha W_2C$ , and  $\beta W_2C$  either as mixtures or single phase materials.

### (3) Amorphous or Glassy Metals

Part of Thrust on Synthesis, Characterization and Properties of  
Noncrystalline Metallic Alloys

Professional Associates: C. R. Barrett, A. I. Bienenstock,  
G. Ilonca, D. L. Keith, G. M. Pound,  
D. A. Stevenson

Graduate Students: Z. S. Jan, G. M. Michal, N.-H. Tsai

Synthesis of amorphous or glassy metals requires rapid quenching rates, the magnitudes of which are determined by the particular alloy being studied. Typical rates for mechanical cooling (splat, spin or brine-quench) varies from  $10^4$  to  $10^9$ °K per second. Lower quenching rate materials can be formed in bulk form in the glassy while materials requiring the higher rates can only be synthesized in thin sections by mechanical cooling. The process used in our work is termed vapor quenching and produces the largest quenching rates obtained during formation of a solid. In thermal physical vapor deposition the energy of the vapor is typically that of the source,  $10^3$ °K. When an atom in this vapor is incident on a surface, it reaches equilibrium within 10 to 15 atomic jumps or approximately  $10^{-12}$  seconds. Therefore, the effective quenching rate is  $10^{15}$ °K per second. A similar analysis yields a quenching rate of  $10^{15}$  to  $10^{18}$ °K per second for sputter deposited materials. These rates are from 5 to 9 orders of magnitude larger than those obtainable by mechanical means.

The goals of this research during the past year and a half were to develop processes for the synthesis of large area ( $70\text{ cm}^2$ ) thick (10-50  $\mu$ ) glassy metals samples. Four specific tasks were undertaken: (a) develop techniques for sputter deposition of alloys of predictable composition and varying composition in the glassy state, (b) apply magnetron sputtering equipment to the synthesis of glassy metals, (c) perform a study of a known system comparing results obtained by vapor quenching with those obtained by mechanical means, and (d) develop capabilities for synthesizing glassy samples from a wide range of elements particularly in binary and ternary form.

Techniques for deposition of samples having known graded composition and predictable uniform composition using both standard RF sputtering and magnetron sputtering techniques have been developed.



Demonstration experiments using alloy systems including niobium-nickel, vanadium-silicon, and copper-silver have been performed. It was demonstrated in this work that the parameter controlling retention of the amorphous state was the substrate temperature during the deposition process. In RF sputtering equilibrium temperatures for the substrate varied from 270 to 350°C at power levels approximately 1 kw. With magnetron sputtering it was observed that the substrate temperatures remained below 60°C during the deposition process and that deposition rates an order of magnitude larger than those obtainable with standard RF sputtering were obtained.

The system studied to compare with results obtained by mechanical means (splat quenching) was the niobium-nickel alloy system. It was observed in this work that the range over which 100% glassy material was retained in vapor quenched samples was approximately 2.5 times larger than that found with splat quenched samples. Also, the range over which any glassy material is formed by vapor quenching is 1.5 times larger than that observed with splat quenched samples. These results were obtained at a substrate temperature of 300°C. The implication of these observations is that the vapor quench process is an extremely powerful tool for synthesizing experimental materials for the study of the glassy state in metals and also of technological interest.

The range of composition over which the glassy state was observed in the niobium-nickel system was from Nb-25at%Ni to Nb-90at%Ni. Measurements of nearest neighbor distances in the glassy state over this composition range followed a straight line behavior interpreted as obeying a Vegard's type law in the glassy metal state. The end points of this curve describe the amorphous state for the pure elements. If the approach of Pauling, which relates distance of closest approach to coordination number, is used to determine coordination number at the observed nearest neighbor spacings, seven nearest neighbors are predicted. Similar results are found with Ag-Cu glassy alloys except that the calculated coordination number is 9.5 to 10, in agreement with observations on liquids of face centered cubic metals. The implication of this Vegard's law behavior for the distance of closest approach in these

alloys is that they may be quasi-ideal solutions, greatly simplifying description of their thermodynamic behavior.

#### (4) Optically Active Conducting Films

Professional Associates: J. F. Gibbons, D. L. Keith

Graduate Student: A. Gat

In this program the main aim is to understand the optical and electrical properties of  $\text{In}_3\text{O}_2/\text{SnO}_2$  with the weight ratio of 95:5. This particular material is interesting because of the combination of DC conductivity with the transparency in the optical region. Its use might be found in the area of solar cells for fabrication of a transparent electrode and creation of particular optical coatings for various purposes.

In the first stage of the project the following properties will be investigated: (a) the conduction mechanism at the low frequencies; (b) the relation of this conductivity to the index of refraction of the material; (c) the possibility of tailoring the optical properties of the oxide layer by changing the preparation procedure of the film.

To achieve these purposes a very uniform Indium Tin Oxide must be sputtered on silicon or on glass. At the outset we wish to perform these experiments at room temperature to minimize any noncontrollable effects on the film properties. A tight cooperation should be established between the investigators and the fabrication group of CMR in order to come close to these tight specifications such as high purity and good homogeneity of the sputter deposited oxide films.

#### (5) Control of Growth Morphologies for Metal Films Deposited at Temperatures Less than 0.3 $T/T_m$

Professional Associate: D. L. Keith

Thick films of several metals were synthesized by magnetron sputter source deposition to study the effects of sequential deposition of the materials in a layered structure on resulting grain size and microstructure. Substrate temperatures between  $0.2 T_{mp}$  and  $0.6 T_{mp}$  of the major constituent were used. This temperature range spans those reported by B. A. Movchan and A. V. Demchishin<sup>(1)</sup> and J. A. Thornton<sup>(2)</sup>

in which the structure of the vapor deposited films varied from a columnar or dome shaped porous grain structure at low substrate temperatures, to a fully dense columnar structure at intermediate temperatures, to a large grained fully dense equiaxed structure at higher temperatures. In the work reported, films of copper layered with niobium were deposited. Thickness of the niobium and copper layers was varied from 20Å to 10,000Å. It was observed that at temperatures at which columnar grains or large equiaxed grains were reported for pure metals, that fully dense fine grain deposits were synthesized by this approach.

It has been found that the deposits are strongly textured (Cu -  $\langle 111 \rangle$ ; Nb -  $\langle 110 \rangle$ ) normal to the plane of the film. Also, grain size is equal to the layer thickness for layers thinner than 1,000Å where Scherrer broadening was used to measure particle size. The most significant result of this work is that fully dense films (25  $\mu$  thick) can be synthesized at substrate temperatures where very porous films are formed by normal continuous evaporation. Also, surface roughness is of the order of half the layer thickness of the thickest layer allowing very smooth films to be formed.

#### Reference Publications:

1. B. A. Movchan and A. V. Demchishin, Fiz. Met. Metalloved. 28, 653 (1969).
2. J. A. Thornton, J. Vac. Sci. Technol. 12, 830 (1975).
3. T. W. Barbee, Jr. and D. L. Keith, "Grain Refinement of Thick Vapor Deposited Films by Sequential Deposition of Dissimilar Metals", presented at Int. Conf. of Metallurgical Coatings, San Francisco (April 1976).

#### (6) Effects of Substrate Morphology and Angle of Incidence of the Vapor Stream on the Morphology of Thick Deposits

Professional Associate: D. L. Keith

Films of nickel, niobium, copper and aluminum deposited onto substrates of characterized surface morphology at angles of vapor incidence varying from a few degrees to normal (90°) have been formed by

vapor deposition using electron beam heated sources and sputter sources. These films were characterized by scanning electron microscopy, x-ray analysis and optical microscopy. In general, it was observed that at angles between the substrate surface and the vapor stream of less than 45° porous columnar growth was typical. The nucleation and development of this porous columnar structure was found to be strongly affected by the surface morphology of the substrate being suppressed by increasing substrate smoothness except at very low angles of vapor incidence. Columns over 50 microns in length have been formed with the dependence on substrate structure indicating that spacing and diameter are primarily controlled by nucleation through surface roughness caused shadowing. These structures are efficient optical absorbers, acting as Mie scatterers and producing efficient, large, area, stable thermal solar energy transducers. In addition, specific surface areas in excess of one meter square per gram have been synthesized.

Reference Publication:

1. T. W. Barbee, Jr. and D. L. Keith, "Effects of Substrate Morphology and Angle of Incidence of the Vapor Stream on the Morphology of Thick Deposits", presented at Int. Conf. of Metallurgical Coating, San Francisco (April 1976).

(7) New Technique for Synthesis of Structures Layered on the Atomic Scale

Professional Associate: D. L. Keith

Techniques have been developed for synthesis, by phase vapor deposition, of layered structures of elemental materials having experimentally determined layer thicknesses varying from 7Å to 1,000Å. In the work to date high rate magnetron sputter sources have been used in a sequential deposition mode implemented with multiple sources and a moving sample. The use of magnetron sputter sources is primary in this process as the energy of the incident ions, the energy deposited into the sample, and the substrate temperature are controlling the stabilization of the layer structure.

Analysis of the structures formed has been primarily by x-ray diffraction. Copper-niobium structures 2 to 25  $\mu$  in total thickness

with a constant niobium layer thickness of 5-30Å and copper layer thickness of from 5-5000Å have been synthesized. Sidebands about the copper <111> diffraction peak have shown the periodicity of the layers to be in agreement with the synthesis process parameters. Particle size analysis showed the niobium and copper layers to consist of grains equal in size to the individual layer thicknesses for layers thinner than 800Å.

Layered samples of tungsten and carbon have also been synthesized in order to explore the low angle diffraction grating behavior of such structures. Carbon and tungsten were chosen to maximize the difference in the atomic scattering factors which, under the forward scattering conditions of these experiments, are approximately 6 and 74, respectively. The results of a continuous diffraction scan using Bragg conditions for a sample consisting of 100 layer pairs of W-80Å and C-20Å taken using Cu-K $\alpha$  radiation showed strong diffraction effects in the  $2\theta$  range 1 to 10°. These results at low angles- $2\theta$  are interpretable in terms of normal diffraction grating theory and analysis showed the layer pair thicknesses to be approximately 110Å in agreement with the synthesis process which was for layer pairs of total thickness 100Å.

These results indicate that layered structures of widely dissimilar materials can be synthesized with layers defined to atomic spacing level (5Å). This allows materials, in their elemental forms, to be brought into intimate contact in ways not previously possible. Results to date have demonstrated that diffraction gratings of known period for x-rays can be synthesized from an extremely wide range of materials. It is expected that similar results can be attained for UV radiation, allowing design and construction of high quality diffraction gratings for this spectral region. Such structures can also be used as neutron diffraction gratings and neutron polarizers if magnetic materials are used.

In addition, the structures formed have many other possible applications. Grain size is, from the work to date, determined by the layer thickness allowing refinement of grain size to levels not normally considered. Further, the layered structures are analagous to spinodal structures typically observed in alloys exhibiting solid state

miscibility gaps, but in an idealized form. The mechanical properties of such structures are expected to be significantly unique to warrant investigation to ascertain technological significance.

The electrical and magnetic properties of these structures will also be of interest. Materials of controllable saturation magnetization, in plane anisotropy, and other significant characteristics can be synthesized. Structures of interest relative to high temperature superconductivity can be synthesized and theories concerning such structures investigated by experiment.

The results to date indicate a new method for the synthesis of layered structures has been developed. It has, at this time, been demonstrated that bulk samples (5 cm x 10 cm x 0.0025 cm) can be synthesized with control of layer thickness to within  $3\text{\AA}$  and reproducibility between layers of the same order. Further, the nature of the synthesis process allows scaling up to larger areas with technological ease.

5. CONTINUUM THEORY OF LATTICE DEFECTS, FRACTURE, AND SURFACE WAVES  
IN ANISOTROPIC ELASTIC MEDIA

D. M. Barnett, Associate Professor, Materials Science and Engineering  
and Division of Applied Mechanics

Graduate Students:

S. D. Gavazza\*  
W. H. McConnell\*  
J. G. Slater  
L. S. Hsu

E. M. Olsen  
J. B. C. Hunter  
B. P. J. Yen

\*Received PhD during report period.

Agency Support:

NSF through CMR  
U.S. Geological Survey 14-08-0001-15260  
EPRI RP 609-1  
NSF/MRL through CMR - Thrust Research Program on the Application  
of the Finite Element Method to the Study of Deformation  
and Fracture of Metals

Technical Objectives:

(1) To produce new straight forward methods for studying the effects of elastic anisotropy on static and dynamic fracture mechanics, on the elastic fields of inclusions, dislocations, and point defects, on surface wave and other steady state wave propagation.

(2) To produce efficient computer schemes for generating diffraction contrast patterns for defect identification.

(3) To study applications of singular dislocation theory to the modeling of geophysical phenomena.

(4) To study inhomogeneous plastic deformation in polycrystalline metals using the finite element method.

Research Report:

1. Forces on Dislocations

Graduate Student: S. D. Gavazza

The proper definition and prescription of the self-force on a plane dislocation loop element tending to move arbitrarily in its plane and normal to its plane has been achieved, thus resolving

a difficulty which had lain unresolved in the literature for over two decades.

2. Effective Elastic Moduli of Deformable Heterogeneous Solids

Graduate Student: W. H. McConnell

A rigorous analysis has been completed to show how the macroscopic response of a heterogeneous solid (laminated composite medium) is obtained by replacing the real discontinuous elastic moduli by simple "effective elastic constants"; the results are universal in that they are valid for any body geometry and external loading. Thermoelastic effects are also included.

3. Defect Identification Using Computer Simulation

Graduate Student: W. H. McConnell

A proof has been given of the uniqueness of defect identification (Burgers vector determination) using computer simulation of electron micrographs of diffraction contrast from dislocations.

4. Surface Waves in Elastic and Piezoelectric Media

(with Professor J. Lothe, Oslo University, Oslo, Norway)

A proof of existence conditions for surface waves in elastic and piezoelectric media has been given.

5. Singular Dislocation Theory Applied to Geophysical Phenomena

Graduate Students: L. S. Hsu and B. Yen

Dislocation models of strike slip, dip slip, and buried faults have been proposed to explain measured surface deformation. Viscous creep beneath a crustal fault has been investigated for a power-type slip-stress law.

6. Finite Element Modeling of Polycrystalline Deformation

Graduate Student: J. Slater

A finite element scheme combined with linear programming methods is being used to computer simulate the deformation of a polycrystalline aggregate including anisotropy of slip, work hardening, and grain boundary compatibility.

7. Acoustic Techniques in Non-Destructive Testing



Graduate Student: J. Hunter

Phase contrast and attenuation measurements on notched samples under load and specimens with contained zones of plasticity are being made as part of an effort to assess residual stress and strain states in deformed samples of structural materials.

Thrust Research Program: A Finite Element Simulation of the Elastic-Plastic Deformation of a Polycrystalline Medium

Graduate Student: J. G. Slater

A finite element program has been written to simulate the elastic-plastic deformation of a polycrystalline sample. The program is able to incorporate the features of anisotropic crystallographic slip into the simulation and to properly treat grain boundary compatibility requirements. A linear programming routine combined with the principle of maximum work will be used to optimally select active slip systems during incremented deformation. In this fashion, the macroscopic stress-strain curve of the deforming polycrystal will be generated and the effects of grain size and texture will be studied.

#### Reference Publications:

1. H. I. Aaronson, M. G. Hall, D. M. Barnett and K. R. Kinsman, The Watson-McDougall Shear: Proof that Widmanstätten Ferrite Cannot Grow Martensitically, Scripta Metallurgica, 9, 705 (1975).
2. J. Lothe and D. M. Barnett, On the Existence of Surface Wave Solutions for Anisotropic Elastic Half-Spaces, Journal of Applied Physics, 47, #2, 428 (1976).
3. S. D. Gavazza and D. M. Barnett, The Image Force on a Dislocation Loop in a Bounded Elastic Medium, Scripta Metallurgica, 9, 1263 (1975).
4. S. D. Gavazza and D. M. Barnett, The Self-Force on a Planar Dislocation Loop in an Anisotropic Linear Elastic Medium, Journal of Mechanics and Physics of Solids (in press).

5. L. B. Freund and D. M. Barnett, A Two-Dimensional Analysis of Surface Deformation Due to Dip-Slip Faulting, Bulletin of the American Seismological Society (in press).
6. J. Lothe and D. M. Barnett, Integral Formalism for Surface Waves in Piezoelectric Crystals, Journal of Applied Physics (in press),
7. R. J. DiMelfi, W. D. Nix, D. M. Barnett, J. H. Holbrook, and G. M. Pound, An Analysis of Thermally Activated Dislocation Motion Based on the Theory of Thermoelasticity, Physica Status Solidi (b) (in press).
8. R. J. Asaro and D. M. Barnett, Applications of the Geometrical Theorems for Dislocations in Anisotropic Media, in Proceedings of a Conference on Computer Simulation for Materials Applications, National Bureau of Standards, Gaithersburg, Md. (in press).
9. W. H. McConnell, On the Approximation of Elliptic Operators with Discontinuous Coefficients, Ann. Scuola Norm. Sup. Pisa (in press).
10. W. H. McConnell, On Modeling the Aggregate Response of Laminated Thermoelastic Media, Journal of Elasticity (in press).
11. W. H. McConnell, Sufficient Conditions for the Identification of Dislocation Burgers Vectors Using Computer Electron Micrographs, Philosophical Magazine (in press).

6. PHOTOELECTRONIC MATERIALS PHYSICS

Clayton W. Bates, Jr., Associate Professor  
Materials Science and Engineering and Electrical Engineering

Professional Associates:

D. Leniart\*

C. Robbins\*\*

H. R. Greenstein - Visiting Scholar \* with Varian Associates

D. B. Leiser - Research Associate \*\* with Diagnostics Information, Inc.

Graduate Students:

D. Das-Gupta

L. Galan

O. L. Hsu

A. McHale

A. M. Salau

M. C. Wu

C. H. Cheng

Agency Support:

ARPA through CMR

Army Research Office (Durham) DAHC-04-73C-0003

NASA NGR 05-020-710

NASA NGR 2102

Technical Objectives:

To investigate the structural, electronic and optical properties of crystalline and amorphous photoelectronic materials in an effort to understand the underlying phenomena with the aim of using these materials in photoelectronic imaging devices such as low light level sensing systems, photomultiplier tubes, etc., and for use in x-ray image intensification and detection applications such as diagnostic radiology. This investigation has been expanded to include the interaction of intense radiation fields with matter.

Approach:

Since the approach to each system investigated will depend upon the use that the system will be put to in a particular device or system, each system will be approached differently and is described accordingly.

Research Report:

(1) Optical Light Shifts in Resonant Excitation Processes

Professional Associate: H. Greenstein

Resonant excitation is highly efficient if the radiation source is coherent and has high spectral brightness. This fact has been recognized in the application of lasers to resonance excitation studies in spectroscopy and photochemistry, and to proposals for separating isotopes. What has not been recognized is the fact that at the flux levels generally contemplated, and readily available from many types of lasers, the radiation may modify the energy level structure of the atom or molecule being irradiated, with attendant modifications in the optical resonance frequencies and the efficiency of transfer to the excited state. For selective excitation, wherein one species is to be excited while another species remains unexcited, these "light-shift" effects will alter the yield and selectivity of the process.

The existence of light-shifts and their significance in the microwave region is well established. What is measured is the shift of a ground-state microwave transition frequency (between hyperfine levels) when the sample is subject to optical pumping. For alkali atoms the shift of the hyperfine levels, and hence of the microwave transition frequency, is generally on the order of 1 Hz per microwatt/cm<sup>2</sup> of incident flux (the exact value of the shift parameter may vary over several orders of magnitude for different substances); since optical pumping is generally done with incoherent sources emitting 1-100 microwatts/cm<sup>2</sup>, these shifts are small. However, the individual level shifts are directly proportional to the radiant flux. It is therefore evident that such shifts can become significant in terms of optical transitions at flux levels that are surprisingly modest by the standards of coherent light sources. For example, for the above shift parameter, the shift will approach 1 GHz (optical Doppler widths are generally less than a few GHz) for a radiation flux of only 10<sup>3</sup> watts/cm<sup>2</sup>. At 10<sup>6</sup> watts/cm<sup>2</sup> level shifts could amount to as much as 10<sup>12</sup> Hz (which is the frequency of a 300 micron molecular vibration-rotation transition in the far infrared).

Thus it is clear that for radiation fluxes of these magnitudes the radiation itself may exert a strong influence on the optical transition frequencies, with the earlier-mentioned consequences. It may also be noted that the line-shift effect, which is proportional to intensity, always dominates over power broadening of the atomic line, which increases only as the square root of intensity.

The focus of this work is therefore what we have termed "optical light shifts", to indicate the fact that our interest is the shift in optical transition frequencies that is induced by radiation whose flux exceeds  $10^3$  watts/cm<sup>2</sup>, approximately. This is to be contrasted with conventional light-shift effects, which modify hyperfine transition frequencies in the microwave part of the spectrum, for optical pumping fluxes on the order of microwatts/cm<sup>2</sup>. This work is presently unfunded but proposals have been submitted to various government agencies.

(2) Luminescence from Bound Excitons in CsI

Graduate Student: A. M. Salau

Research Associate: D. Leniart

This work is a continuation of last year's work on absorption, excitation and emission spectra of pure CsI which had not been exposed to ionizing radiation and which was relatively strain and defect free. This work has been extended to cover the range from room to liquid helium temperatures in a continuous fashion. In addition electron spin resonance (ESR) experiments have been performed over this same temperature range to complement the optical studies.

Bulk single crystals were used in the photoluminescence and ESR experiments and both bulk single crystals and thin films 500Å-2000Å thick were employed for taking the ultraviolet absorption data. At room temperature before cooling no emissions or ESR signals were observed for any of the samples investigated. As the temperature was lowered to that of liquid nitrogen two emissions with  $\lambda_{\text{max}}$  at 420 and 350nm appear for excitation in the 205-235nm range, i.e., from the excitonic region to the long wavelength tail of the fundamental absorption. The 350nm emission is excited most efficiently in the excitonic region

205-225nm, whereas the 420nm emission is more readily produced by excitation in the long wavelength tail of the fundamental absorption at 235 nm. This general behavior continues down to liquid helium temperatures. At the temperature of liquid helium ( $4.2^{\circ}\text{K}$ ) an emission at  $2900\text{\AA}$  appears under excitation in the excitonic region and disappears at  $\sim 25^{\circ}\text{K}$ . This emission has been observed by other workers and will not be dealt with here.

An interesting effect has been observed when the samples are temperature cycled between room and liquid nitrogen and lower temperatures. Emissions which were not present at room-temperature-before-cooling (RTBC) appear in the 350-550nm range depending on the excitation wavelength. It has been found that the intensities of these room-temperature-after-cooling luminescences (RTAC) are approximately 30-40 percent stronger when the samples are exposed to radiation in the 205-235nm range when at the lower temperatures before warming back to room temperature, relative to samples which were not similarly exposed.

ESR data was taken on pure single crystals of CsI and single crystals of CsI doped with thallium (0.1 mole percent) and sodium (0.01 mole percent). Experiments were performed on the doped samples which are known from previous studies to produce stable hole centers at liquid nitrogen temperatures to compare with the pure samples which under conditions of high gain hint at the presence of an anisotropic hole-like paramagnetic center. At room temperature the pure samples showed no ESR signals. Cooling slowly to about  $80^{\circ}\text{K}$  produced an ESR signal described by magnetic parameters indicating the presence of an F center. The signal is characterized by a g-value of  $2.003 \pm .001$  with a peak-to-peak line width of 100 Gauss and is isotropic in nature. The signal intensity increased as the temperature was lowered to  $80^{\circ}\text{K}$  and changed very little between  $80^{\circ}\text{K}$  and  $20^{\circ}\text{K}$ , the maximum amplitude occurring between  $60^{\circ}\text{K}$ - $70^{\circ}\text{K}$ , with the signal intensity remaining isotropic. The signal persists upon warming back to room temperature which correlates quite nicely with the optical data. Effects to correlate the hole-like center observed in pure CsI with hole-centers observed in CsI(Tl) and CsI(Na) were only moderately successful.

Using the theoretical model developed by Bassani and Inchauspe for determining the positions of the  $\alpha$  and  $\beta$ -bands in CsI we obtain values of  $235 \pm 5\text{nm}$  and  $224 \pm 2\text{nm}$  respectively for these bands, which coincide with the peaks observed in the excitation spectra for the 350 and 420nm emissions, further suggesting that the observed emissions are due to the annihilation of excitons bound to negative ion vacancies ( $\alpha$ -bands) and excitons bound to F-centers ( $\beta$ -bands). These observations seem to imply that in pure CsI cooling to liquid nitrogen and lower temperatures produces traps for both electrons and holes which do not release them upon warming back to room temperature and that these centers are responsible for the luminescence observed at RTAC. This work has been accepted for publication in Physical Review.

(3) Luminescence Phenomena in CsI(Na)

Graduate Student: O. L. Hsu

The previous year's work on absorption, emission and excitation spectra of CsI(Na) has been extended to include polarization studies of the observed emissions and measurements between room and liquid helium temperatures.

Absorption, emission and excitation spectra of CsI:Na were measured on bulk single crystals and thin films between room temperature (RT) and liquid helium temperature (LHeT). Excitonic absorption peaks as well as absorption in the long-wavelength tail of the fundamental absorption which is not present in pure CsI were observed. In addition to emission at  $4250\text{\AA}$ , excitonic emission at  $3400\text{\AA}$ , normally found at LNT, has also been observed at RT. This room temperature UV emission is closely related to the heat treatment process that the specimen received. Part of this work has been published in the Journal of Luminescence 11, 65 (1975).

(4) Strain-Induced Room Temperature Photoluminescence Studies in CsI and CsI(Na)

Research Associate: I. Schneider<sup>+</sup>

<sup>+</sup> Permanent address, Naval Research Laboratories, Washington, D. C.

Graduate Students: A. M. Salau and O. L. Hsu

The photoluminescence produced from mechanically deformed crystals of pure CsI and the photoluminescence increase of CsI(Na) crystals similarly prepared, where the amount of sodium is considerably less than that required for maximum photoluminescence efficiency was measured. Several interpretations of the results are suggested. We have found that producing strains by deforming the specimen (4% deformation) produced luminescence at 425nm in pure CsI at room temperature which was not present before and increases the luminescence in samples of CsI(Na) at room temperature which does not contain the optimum amount of sodium for maximum luminescence at 425nm. Deforming (4%) samples of CsI(Na) with the optimum amount of sodium (6ppm) produces no change in the emission at 425nm at room temperature.

At present these results are not clearly understood. The 425nm emission strongly resembles the thermoluminescence produced at low temperatures and attributed to the migration of  $V_k$  centers followed by the radiative recombination with electrons trapped at sodium sites. However, it is uncertain both why the intensity of the emission at room temperature decreases for  $Na^+$  concentrations in excess of 6ppm or why deformation (or thermal quenching) has such a pronounced effect on the intensity unless these treatments have a dissolution effect on sodium or other structural clusters already present in the lattice. Yet another possibility is that the deformation (or thermal) treatments may so substantially increase the mobility of the irradiation produced  $V_k$  centers that even the trace amounts  $Na^+$  present in the crystal are now quite effective as recombination sites. A more detailed investigation now underway hopefully will shed some light on this matter.

This work has been published in Solid-State Communications 18, 101 (1976).

(5) Divitrification Studies of High Purity Silica Fibers

Graduate Student: A. E. McHale

During this period, 10/75 - 5/76, we have conducted a thorough survey of the literature to determine the state-of-the-art in the area



of glass ( $\text{SiO}_2$ ) - alkali interaction. Due to the nature of the fibrous material under investigation and the many aqueous environments it sees during processing of the RS1 material, a model has been developed of the fiber surface and its interaction with these environments, including the alkali cations.

The necessary equipment has been assembled and experiments are being designed to test this model of the surface under controlled conditions. It is expected that the results of these experiments will yield basic information necessary for the understanding of the formation of the fiber surface and its effect upon observed devitrification behavior of the fiber in RS1 material.

#### (6) Optical Properties of Fused Silica in Intense Radiation

Graduate Student: M. C. Wu

Entries into the atmospheres of the outer planets such as Saturn, Uranus and Jupiter, produce a much higher heat flux compared to earth entry, which changes the heat transfer mode to the heat shield from convective to mostly radiative heating. This change to radiative heat transfer potentially makes a reflective heat shield more efficient and therefore more attractive from a weight savings standpoint than a conventional ablative heat shield, such as carbon-phenolic. This is of significance for planetary entry since the heat shield weight is from 30 to 50 percent of the weight of a planetary probe vehicle.

The concept of a reflecting and ablative heat shield was demonstrated using Teflon in 1971. It is the purpose of this program to extend this work by utilizing high purity silica in its various forms to produce a useful, actual heat shield material which could be used for planetary entry. Silica was selected as a promising candidate material because it has a high reflectance of the incident radiation, is a good ablator, has excellent resistance to thermal stress and is available in various forms.

In this program various forms of silica were evaluated as well as various processing methods for fabricating the heat shield. In the technical evaluation of various silicas one of the goals was to provide

data and knowledge on how the key properties for a silica reflective heat shield vary as a function of the controllable and important silica material and processing variables.

At Stanford our work is of a theoretical and experimental nature. The experimental work is involved with determining the ablative species (charged and uncharged) under various incident radiations using a time-of-flight mass spectrometer at the NASA-Ames facility. This work is just starting. The theoretical work has involved determining the absorption coefficient  $\alpha(\text{cm}^{-1})$  as a function of temperature in the edge region ( $\sim 2000 \text{ \AA}$ ). This work has been aided by calculations performed at the Palo Alto research laboratories of Xerox, whose workers show that the vibrational spectrum of  $\text{SiO}_2$  is roughly independent of whether the material is amorphous or crystalline. The shift of the absorption edge with temperature for fused silica has been measured by a number of researchers and they show a linear dependence of the edge with temperature which one expects for crystalline materials and supports the theoretical work. One is thus able to closely approximate the absorption edge by an Urbach type of temperature dependence which one can use in the radiative transfer equations to determine the natural behavior under intense radiation.

(7) Photoelectron Spectroscopy of Multialkali Photoemitting Surfaces

Graduate Students: L. Galan and D. Das Gupta

This work is in the second year of a three year grant from the Army Research Office at Durham on Basic Studies of High Performance Multialkali Photoemitters. The first year was devoted to investigating the effects of various substrates on multialkali photoemitters performance (band-bonding, etc.) employing a conventional processing station (base pressures  $\sim 10^{-8}$  Torr). None were found that could be determined with this step.

This year we have concentrated on building an ultrahigh vacuum system ( $10^{-11}$  Torr) for performing UV photoemission and ESCA studies on the photoemitters during processing to enable us to hopefully distinguish between average multialkali photoemitters ( $300 \frac{\mu\text{a}}{\text{lumen}}$ ) and

"super"ones (500-700  $\frac{\mu\text{a}}{\text{lumen}}$ ).

#### Reference Publications

1. C. W. Bates, Jr., "New Trends in X-ray Image Intensification", Proc. of Society of Photo-Optical Instrumentation Engineers 47, 152 (1975).
2. C. W. Bates, Jr. and Stephen Sparks, "Modulation Transfer Function of a 210/70mm Fibre-Optic Output X-ray Image Intensifier Tube", Applied Optics Letters, 14, 1484 (1975).
3. C. W. Bates, Jr. et al, "Optical Properties of CsI(Na) and Heat-Treated Pure CsI", Physics Letters, 51A, 425 (1975).
4. C. W. Bates, Jr. et al, "Strain-Induced Room Temperature Photoluminescence in CsI and CsI(Na)", Solid State Communications 18, 101 (1976).
5. Olive Lee Hsu and C. W. Bates, Jr., "Luminescence Phenomena in CsI(Na)", Jour. of Luminescence 11, 65 (1975).
6. C. W. Bates, Jr. et al, "Luminescence from Bound Excitons in CsI", (accepted for publication in Physical Review).
7. H. Greenstein and C. W. Bates, Jr., "Linewidth and Tuning Effects in Resonant Excitation", Jour. Opt. Soc. 65, 33 (1975).

## 7. ELECTROMAGNETIC PROPERTIES OF SUPERCONDUCTORS

M. R. Beasley, Associate Professor, Applied Physics and Electrical Engineering

### Graduate Students:

D. F. Moore  
S. T. Ruggiero  
R. B. van Dover

### Agency Support:

JSEP  
NSF DMR 75-04368  
NSF/MRL through CMR

### Technical Objectives:

To extend and deepen the understanding of the electromagnetic behavior of superconductors and superconducting structures and devices.

### Approach:

The response of superconductors to currents, magnetic fields, and electromagnetic radiation under a wide variety of conditions are studied and related to the basic properties, structure, material parameters, and geometry of the superconductors. Tunneling studies to determine microscopic electronic properties of superconductors.

### Research Reports:

- (1) Tunneling Studies of  $\text{Nb}_3\text{Sn}$  and Other A-15 Superconductors

Graduate Student: D. F. Moore

Oxide-layer tunnel junctions exhibiting both quasi-particle and Josephson tunneling have been produced on electron beam codeposited  $\text{Nb}_3\text{Sn}$  thin films. The I-V characteristics are superior to any attained previously. The superconducting energy gap  $\Delta$  has been studied as a function of composition and found to increase with increasing Sn concentration from 19% atomic percent Sn through stoichiometry to about 29% Sn where the material enters a two-phase region. The lack of a well defined peak in  $\Delta$  at stoichiometry is unexpected and of possible fundamental significance. The heating problem at large bias currents noted earlier has been eliminated and characteristics suitable for phonon density of states and electron phonon interaction studies

have been obtained. Such studies are now under way.

Reference Publication:

D. F. Moore, J. M. Rowell, and M. R. Beasley, "Superconductive Tunneling Into Niobium-Tin Thin Films," (to appear in Solid State Communications).

(2) Vortex Penetration into High-K Superconducting Films

Graduate Student: D. F. Moore

Using the tunnel junctions described in (1) above, we have studied the flux penetration process in films of  $\text{Nb}_3\text{Sn}$  by measuring the effect of a parallel applied field on the I-V characteristics as a function of film thickness. We find the change in the I-V curve becomes irreversible at a characteristic field which we associate with flux entry. This field increases markedly with decreasing film thickness as expected. However even in thick films ( $\sim 1\mu\text{m}$ ) we find flux penetration is delayed to fields of  $\sim 2000 \text{ Oe}$ , much larger than  $H_{c1}$ . This indicates a large surface barrier to flux penetration is operative in these films. This barrier is of practical concern in superconducting power transmission conductors as well as in theories of the metastability of the Meissner state.

Reference Publication:

D. F. Moore, M. R. Beasley, and J. M. Rowell, "Tunneling Studies of  $\text{Nb}_3\text{Sn}$  Films in Parallel Magnetic Fields," Bul. Am. Phys. Soc. 21, 403 (1976).

(3) High- $T_c$  Superconducting Microbridges

Graduate Student: R. B. van Dover

Moderately small  $2\mu\text{m} \times 2\mu\text{m} \times 0.05\mu\text{m}$  microbridges of  $\text{Nb}_3\text{Sn}$  have been produced by various means. Geometry definition by anodization has proven most satisfactory, producing excellent edges. Ion milling has been found to drastically reduce  $T_c$ , apparently by producing disorder in the entire bridge, even though the ions strike the material only at the edges. Geometrically these are the best high- $T_c$  microbridges made to date. Unfortunately they do not show consistent behavior in their I-V characteristics suggesting some material nonuniformities may be present. However, better  $\text{Nb}_3\text{Sn}$  films (as evidenced by oxide layer

tunneling studies) are now available and small microbridges are expected soon through electron lithography. The combination of these two improvements should lead to more consistent electrical behavior in these junctions.

(4) Superconducting Layered Structures

Graduate Student: S. Ruggiero

Theoretical work reported earlier has predicted a dimensional crossover from 3-D to 2-D in superconducting layered compounds (e.g.  $\text{TaS}_2$  (pyridine) $_{\frac{1}{2}}$ ) as  $T$  is reduced below  $T_c$ . This crossover is associated with the fact that at low temperatures the Ginzburg-Landau coherence length of these materials along the  $c$ -axis can become small compared to the layer separation. Anticipated consequences of this situation on the vortex dynamics (or possible Josephson behavior) in these materials is now being sought experimentally. Results are not yet available, but the necessary equipment is being assembled.

Reference Publication:

R. A. Klemm, A. Luther, and M. R. Beasley, "Theory of the Upper Critical Field in Layered Superconductors," Phys. Rev. B 12, 877 (1975).

## 8. STRUCTURES OF AMORPHOUS MATERIALS

A. I. Bienenstock, Professor, Materials Science & Engineering and  
Applied Physics

### Professional Associates:

J. B. Hastings  
S. C. Rowland

### Graduate Students:

D. J. HaferBurns\*  
S. H. Hunter

\*Received M.S. during report period.

### Agency Support:

NSF DMR73-02356 A01  
NSF GH40785  
NSF/MRL through CMR

### Technical Objectives:

To investigate atomic arrangements in amorphous materials in an effort to understand thermal, crystallization, electronic and vibrational properties.

### Approach:

The two basic methods used during the past year were x-ray diffraction radial distribution and extended x-ray absorption fine structure analyses.

### Research Report:

- (1) Extended X-ray Absorption Fine Structure (EXAFS) Studies of Amorphous Materials

Graduate Student: S. H. Hunter

During the past year, new EXAFS data from samples of crystalline Ge, amorphous Ge prepared by glow discharge by J. Knights, amorphous Ge prepared by evaporation, amorphous and crystalline GeSe<sub>2</sub>, as well as glassy Cu<sub>5</sub>As<sub>38</sub>Se<sub>57</sub> were obtained at the Stanford Synchrotron Radiation Project. Our primary efforts were directed, however, at the analysis of EXAFS data from crystalline and amorphous Ge-Se and Cu-As-Se alloys. The former are important because structural interpretations of their radial distributions are quite ambiguous. The

ambiguities lead, in turn, to ambiguities in interpretations of physical properties. The Cu-As-Se glasses were investigated because the addition of Cu to As-Se glasses leads to a marked decrease in the bandgap and a corresponding increase in the electrical conductivity. It was our belief that these changes result from marked changes in the short-range order, which we hoped to characterize.

Computer programs were developed for the extraction of the EXAFS from the experimental data and for the Fourier transformation of the resulting EXAFS. In collaboration with T. M. Hayes and P. N. Sen, the Fourier transformation programs were extended to include a Gaussian broadening of the k-space square window used in the transformation. Using Ge as a test material, the interpretation of the Fourier transform was explored<sup>2,3</sup>.

The studies<sup>4,5</sup> of the Cu-As-Se system indicate that the coordination of Cu in the glasses is quite similar to that of Cu in crystalline  $\text{CuAsSe}_2$ , but with a greater spread in interatomic distances. Of particular importance was the demonstration<sup>5</sup> that the coordination of Cu in glassy  $\text{Cu}_{55}\text{As}_{38}\text{Se}_{57}$  is the same as that in glassy  $\text{Cu}_{25}\text{As}_{30}\text{Se}_{45}$ . This result shows the effectiveness of EXAFS studies for determining the coordinations of low concentration additives in amorphous materials. Such determinations are not achievable normally with radial distribution function techniques.

The studies of amorphous and crystalline  $\text{GeSe}_6$  indicate that the EXAFS are consistent with a structural model in which the Ge is fourfold and the Se twofold coordinated, but not with a model in which each is threefold coordinated. This result appears to resolve the long-standing and important ambiguity in the interpretation of x-ray diffraction radial distribution studies.

Efforts are now underway to determine the reliability of EXAFS coordination number determinations in the amorphous and crystalline Ge-Se systems.

## (2) Structure of Germanium Chalcogenide Glasses

Professional Associate: S. C. Rowland

Graduate Student: D. J. HaferBurns



This work is directed towards understanding the manner in which the short range order in germanium chalcogenide glasses changes with the addition of heavier Group IV elements, as well as understanding the basic structure of glasses close to the composition  $\text{Ge}_2\text{X}_3$ , where X is S or Se. X-ray diffraction radial distribution functions have been obtained, in addition to those discussed in last year's report, for glasses in the Ge-Sn-S and Ge-Pb-S systems.

The results obtained thusfar<sup>7</sup> indicate that the radial distribution function for amorphous  $\text{Ge}_2\text{S}_3$  is consistent with a model in which each Ge is coordinated by one Ge and three S atoms while each S is coordinated by two Ge atoms, as proposed by other workers.

When added to these glasses, the Sn and Pb appear to act as classical network modifiers, rather than being a part of the network. That is, the Sn and Pb are in the glass as positive charge divalent ions. For each such positively charged ion, there are two negatively charged monovalent S ions which are singly coordinated (i.e., non-bridging S ions).

(3) Synchrotron Radiation for Anomalous Dispersion X-ray Diffraction Studies of Amorphous Materials

Professional Associate: J. B. Hastings

As part of the Thrust Program in Glassy Metals, the feasibility of obtaining separate A-A, A-B and B-B pair distribution functions through the use of the anomalous dispersion of x-rays near x-ray absorption edges has been explored extensively. This opportunity arises because of the tunability of the x-rays obtained from a synchrotron radiation source like that of the Stanford Synchrotron Radiation Project. Numerical analyses indicate that the resulting distribution functions will be quite sensitive to experimental error but, when combined with EXAFS analyses, should become extremely important tools for determining atomic arrangements in binary amorphous materials of sufficiently high atomic number. One of the most striking conclusions<sup>6</sup> is that it should be possible to experimentally remove the Compton scattering as a natural part of the anomalous dispersion experiment.

Assembly of the experimental apparatus has been initiated and should be completed soon should funding become available.

Reference Publications and Presentations:

1. A. Bienenstock, F. Mortyn, S. Narasimhan and S. C. Rowland, "X-Ray Diffraction Radial Distribution Studies of Glassy  $\text{Ge}_{.42}\text{Se}_{.58}$  and  $\text{Ge}_{.2}\text{As}_{.3}\text{Se}_{.5}$ ", in Frontiers in Materials Science, edited by L. E. Murr and C. Stein (Dekker, 1976), p.1.
2. T. M. Hayes, P. N. Sen and S. H. Hunter, "Interpreting EXAFS in Real Space", to be published in the Proceedings of International Topical Conference on Structure and Excitations of Amorphous Solids, Williamsburg, Va., March, 1976.
3. T. M. Hayes, P. N. Sen and S. H. Hunter, "Structure Determination in Real Space: Ge", submitted for publication in J. Phys. C.
4. S. Hunter and A. Bienenstock, "EXAFS Studies of Glassy  $\text{CuAsSe}_2$  and  $\text{Cu-As}_2\text{Se}_3$  Alloys", to be published in the Proceedings of the Sixth International Conference on Amorphous and Liquid Semiconductors, Leningrad, USSR, November, 1975.
5. S. H. Hunter and A. I. Bienenstock, "EXAFS Studies of Amorphous Semiconductors", Bull. Amer. Phys. Soc. 21, 309 (1976).
6. A. Bienenstock, "Applications of Synchrotron Radiation to the Study of Amorphous Materials", Bull. Amer. Phys. Soc. 21, 676 (1976), invited paper.
7. D. HaferBurns, A. Bienenstock and S. C. Rowland, "Radial Distribution Studies of Ge-Sn-S and Ge-Pb-S Glasses", Bull. Amer. Phys. Soc. 21, 467 (1976).

## 9. PROPERTIES OF ADSORBENTS AND CATALYSTS

M. Boudart, Professor, Chemical Engineering and Chemistry

### Professional Associates:

J. E. Benson  
J. M. Criado  
R. A. Dalla Betta  
A. L. Frennet

E. L. Kugler  
G. I. Panov  
S. Yoshida

### Graduate Students:

B. L. Beegle  
F. V. Hanson\*  
H. S. Hwang\*  
S. Ladas\*\*  
Y. L. Lam  
K. J. Lim

C. L. McConica \*\*  
M. L. Murtiff  
D. J. O'Rear  
D. C. Silverman\*  
R. S. Weber

\*Received PhD during report period

\*\*Received MS during report period

### Agency Support:

NSF GP 42186  
NSF GK 17451X  
NSG ENG 74-22234  
ARPA through CMR  
Exxon Research and Engineering Company  
NSF/MRL through CMR - Thrust Program on Alloy Catalytic Materials

### Technical Objective:

To prepare and characterize finely divided materials and understand their chemical surface reactivity and catalytic activity in selected reactions.

### Approach:

For the synthesis of catalytic materials, the physical chemistry of their preparation and of what follows it, namely the genesis of the catalyst, is studied by means of Infra-Red Absorption Spectroscopy (IRS), electron spin resonance (ESR), Mössbauer spectroscopy (MS), Auger electron spectroscopy (AES), x-ray diffraction (XRD), extended x-ray absorption fine structure (EXAFS) as well as conventional methods of

physisorption, chemisorption and chemical reactivity including catalytic tests. The same methodology is applied to the structural and electronic characterization of the new materials, the final aim being an understanding of their catalytic activity and selectivity in a number of reactions.

#### Research Report:

Small particles of palladium-gold alloys (average size 2 nm) supported on silicagel have been synthesized and characterized. The rate of the catalytic reaction between dioxygen and dihydrogen referred to palladium surface site increases markedly as more gold is substituted for palladium, reaches a sharp maximum in mid-composition range to fall sharply to the very low catalytic rates obtained with pure gold.

The surface composition of reduced iron catalysts used in ammonia synthesis of fuels and chemicals, has been determined by both AES and conventional methods which provide a reliable calibration for the new electron spectroscopy. This quantitative surface analysis provides the first step toward the understanding of the role of impurities (called promoters) added to the metallic iron which is the active element in these catalytic reactions.

Small particles of palladium supported on carbon have been prepared which have twice as much surface palladium than samples available commercially. These samples will be examined for their ability to provide oxygen electrode with higher electrocatalytic activity.

Finally, in the Thrust Program on Alloy Catalytic Materials area, new samples of tungsten carbide powders with crystallite size in the 10 nm range have been prepared, characterized and tested for surface reactivity. The significant conclusion has been reached that excess surface carbon is bad for surface reactivity and this knowledge is now applied to improved preparation methods. Since the final purpose of this work is to understand and control similarities in surface behavior between tungsten carbide and platinum, further work on the behavior of the latter in a simple test reaction is of interest and will be extended to WC powders and single crystals. In the work thus far, the following observations have been made.

When polycrystalline and single crystal surfaces of platinum on which a fraction of a monolayer of oxygen has been pre-adsorbed are exposed at room temperature to  $H_2$  gas at  $<10^{-8}$  Torr, the number of O adatoms removed per collision of an  $H_2$  molecule with the surface is nearly unity, leading to a model for the reaction. By contrast, this reaction probability is only  $10^{-7}$  when  $H_2$  and  $O_2$  react together at the same temperatures but pressures of the order of 10 Torr or more on small particles of platinum supported on silicagel. The results under different conditions will be discussed in the context of the model derived from the experiments mentioned first.

#### Reference Publications:

1. A. Delbouille, J. A. Dumesic, S. Khammouma, H. Topsøe and M. Boudart, "Surface, Catalytic and Magnetic Properties of Small Iron Particles, Part I: Preparation and Characterization of Samples", J. Catal. 37, 486 (1975).
2. J. A. Dumesic, H. Topsøe, S. Khammouma and M. Boudart, "Surface, Catalytic and Magnetic Properties of Small Iron Particles, Part II: Structure Sensitivity of Ammonia Synthesis", J. Catal. 37, 503 (1975).
3. J. A. Dumesic, H. Topsøe and M. Boudart, "Surface, Catalytic and Magnetic Properties of Small Iron Particles, Part III: Nitrogen Induced Surface Reconstruction", J. Catal. 37, 513 (1975).
4. M. Boudart, "Concepts in Heterogeneous Catalysis", in Interactions on Metal Surfaces, R. Gomer, Ed., Chapter 7, Springer Verlag, New York, 1975.
5. E. G. Derouane, V. Indovina, A. B. Walters and M. Boudart, "Preparation of Copper on Magnesia Catalysts: An Electron Spin Resonance Study", J. Catal. 39, 115 (1975).
6. H. S. Hwang and M. Boudart, "Solubility of Hydrogen in Small Particles of Palladium", J. Catal. 39, 44 (1975).
7. J. G. Fripiat, K. T. Chow, J. B. Diamond, K. H. Johnson and M. Boudart, "The Structure and Bonding of Lithium Clusters", J. of Mol. Catal. 1, 59 (1975).
8. M. Boudart, "Heterogeneous Catalysis", Chapter 7 of Physical Chemistry: An Advanced Treatise, Eds., H. Eyring, W. Jost and D. Henderson, Academic Press, 1975.

9. A. Amirnazmi and M. Boudart, "Decomposition of Nitric Oxide on Platinum", J. Catal. 39, 383 (1975).
10. J. A. Dumesic and M. Boudart, "Catalytic Synthesis and Decomposition of Ammonia", in The Catalytic Chemistry of Nitrogen Oxides, Eds., R. L. Klimisch and J. G. Larson, Plenum Publishing Corporation, New York, 1975, p. 95-106.
11. H. Topsøe, J. A. Dumesic and M. Boudart, "Catalytic and Magnetic Anisotropy of Iron Surfaces", in The Physical Basis for Heterogeneous Catalysis, Eds., E. Drauglis and R. I. Jaffee, Plenum Press, New York, 1975, p. 337-362.
12. R. A. Dalla Betta and M. Boudart, "Infrared Examination of the Reversible Oxidation of Ferrous Ions in Y Zeolite", J. Catal. 41, 40 (1976).

## 10. INTRINSIC CHEMICAL REACTIVITY

John I. Brauman, Professor, Chemistry

### Graduate Students:

S. R. Aragon*	H. L. McPeters
O. I. Asubiojo	T. J. O'Leary*
D. R. Bauer*	W. N. Olmstead
C. W. Cornelius	K. J. Reed*
W. E. Farneth*	R. N. Rosenfeld
R. Gooden	A. H. Zimmerman
B. K. Janousek	

\*Received Ph.D. during report period.

### Agency Support:

NSF(MPS 73-08481,CHE 76-02420)

PRF (8712-AC5)

### Technical Objective:

To obtain an understanding and separation of intrinsic (molecular) factors and solvation phenomena which affect chemical reactivity.

### Approach:

We study a variety of chemical reactions both ionic and molecular, in both the gas and condensed phase. Comparison of results allows us to understand intrinsic effects (from the gas-phase) and intrinsic plus solvation effects (from condensed phases).

### Research Report:

#### (1) Gas-Phase Ionic Reactions

##### Graduate Students:

O. I. Asubiojo	B. K. Janousek
W. E. Farneth	W. N. Olmstead
R. Gooden	K. J. Reed
	R. N. Rosenfeld

We have continued our studies of gas phase ionic equilibria in alcohols and thiols, determining relative acidities as well as attempting to relate these acidities to an absolute standard, HF. We have also initiated studies of acidities of a variety of polyenes, ketones, and aldehydes. We have explored in more detail the addition of nucleophiles such as halide ions to carbonyl and sulfonyl centers, measuring rates and identifying intermediates. We have been able to model ion-molecule reactions and are able to predict accurately measured rate constants and their temperature dependence, using only equilibrium data.

(2) Electron Affinities, Photochemistry of Ions

Graduate Students:

R. Gooden	K. J. Reed
B. K. Janousek	A. H. Zimmerman
H. L. McPeters	

By studying thresholds for photodetachment of electrons from negative ions we have obtained estimates for electron affinities of a number of phenoxyl radicals, thiophenoxyl, and benzyl radical. We have preliminary data on a number of new systems including enolates and highly conjugated linear anions. We have developed a theory for cross section behavior which correctly predicts the energy dependence. This can be used to infer geometries and can also provide information on electron distribution.

(3) Isotope Separation

Graduate Student: T. J. O'Leary

Work done in collaboration with Professor Schawlow (Physics). We have been exploring a variety of methods for



isotope separation which make use of some of the unique properties of lasers. Both experimental and theoretical analyses of HBr and Br<sub>2</sub> photodissociation have been carried out.

(4) Light Scattering

Graduate Students: S. R. Aragon  
D. R. Bauer  
C. W. Cornelius

Work done in collaboration with Professor Pecora (Chemistry). We have begun to upgrade our instrumentation, taking advantage of a minicomputer as well as building a variety of interfaces. We have studied some of the effects of weak molecular interactions by measuring the depolarized Rayleigh spectra of mixtures of benzene and hexafluorobenzene. We observe both static and dynamic effects consistent with the non-ideality of these mixtures, but no evidence could be found for dimers which live as long as 10 picoseconds. We have also examined the behavior of a variety of polystyrenes as a function of molecular weight. We find evidence both for internal chain motions and overall molecular reorientation.

(5) Graphite Intercalates

Graduate Student: L. B. Ebert

Work done in collaboration with Professor Huggins (Materials Science). We have continued our studies of reaction products of graphite. Treatment of fluorinated graphite (CF)<sub>x</sub> with strong Lewis acids produces a new substance which may involve positively charged graphite planes with the negatively charged salts of the Lewis acids intercalated.

## Reference Publications:

1. J. H. Richardson, L. M. Stephenson, and J. I. Brauman, "Photodetachment of Electrons from Phenoxides and Thiophenoxide," J. Amer. Chem. Soc., 97, 2967 (1975).
2. J. I. Brauman, "Acid and Base," McGraw-Hill Yearbook of Science and Technology, McGraw-Hill, New York, 1975.
3. J. H. Richardson, L. M. Stephenson, and J. I. Brauman, "Photodetachment of Electrons from Large Molecular Systems. Benzyl Anion. An Upper Limit to the Electron Affinity of  $C_6H_5CH_2$ ," J. Chem. Phys., 63, 74 (1975).
4. D. R. Bauer, J. I. Brauman, and R. Pecora, "Depolarized Rayleigh Scattering and Orientational Relaxation of Molecules in Solution. IV. Mixtures of Hexafluorobenzene with Benzene and with Mesitylene," J. Chem. Phys., 63, 53 (1975).
5. D. R. Bauer, J. I. Brauman, and R. Pecora, "Depolarized Rayleigh Spectroscopy Studies of Relaxation Processes of Polystyrenes in Solution," Macromolecules, 8, 443 (1975).
6. O. I. Asubiojo, L. K. Blair, and J. I. Brauman, "Tetrahedral Intermediates in Gas Phase Ionic Displacement Reactions at Carbonyl Carbon," J. Amer. Chem. Soc., 97, 6685 (1975).
7. J. P. Collman, J. I. Brauman, and K. S. Suslick, "Oxygen Binding to Iron Porphyrins," J. Amer. Chem. Soc., 97, 7185 (1975).
8. K. J. Reed, A. H. Zimmerman, H. C. Andersen, and J. I. Brauman, "Cross Sections for Photodetachment of Electrons from Negative Ions Near Threshold," J. Chem. Phys., 64, 1368 (1976).

# 11. CRYSTAL CHEMICAL STUDIES OF CRYSTALLINE AND AMORPHOUS SILICATES

Gordon E. Brown, Assistant Professor, Geology

## Professional Associate:

P. M. Fenn, Research Associate, Geology

## Graduate Students:

B. G. Aitken

B.H.W.S. de Jong

B. A. Mills

K. D. Keefer

M. P. Taylor

## Agency Support:

NSF GA 41731

## Technical Objectives:

(1) To gain a fundamental understanding of the relationships between a mineral's stability and the variables temperature and composition at the atomistic-electronic level. (2) To obtain information concerning the structure and properties of silicate glasses. (3) To study the nature of mineral intergrowths.

## Approach:

The crystal structures, compositional variations and electronic energies of naturally-occurring and synthetic crystalline silicates are being investigated by a combination of (1) single-crystal and powder X-ray diffraction methods over a range of temperatures (24°-1100°C); (2) X-ray emission microanalysis; (3) transmission electron microscopy; (4) photoelectron spectroscopy; and (5) semiempirical quantum chemical calculations on representative molecular fragments of silicate structures. Estimates of stability differences between various structural perturbations of silicates are obtained by semiempirical molecular orbital and electrostatic energy calculations. Structural variations

in synthetic silicate glasses are being studied by X-ray radial distribution analysis and photoelectron spectroscopy.

Research Report:

(1) X-ray Diffraction Studies of Silicate Structures at Various Temperatures

Professional Associate: P. M. Fenn

Graduate Students: B. A. Mills

M. P. Taylor

Structural studies of rock-forming minerals as a function of temperature yield important information about a number of subsolidus features such as structural expansion, phase transformations, exsolution mechanisms and kinetics, intracrystalline cation exchange, domain structure and thermal motion of atoms. Such information is useful to the earth scientist because of its bearing on mineral geothermometry and interpretation of the thermal history of rocks. For this work we are using high-temperature furnaces, mounted on a precession camera and an automated 4-circle diffractometer, which are capable of continuous operation at temperatures up to 1100°C.

As part of a continuing investigation of the structural and compositional variations of the feldspar minerals, which comprise about 60% of the earth's crust, we have completed a study of the thermal expansion behavior (24°-1000°C) and structural changes with temperature of a synthetic, compositionally intermediate, hypersolvus alkali feldspar ( $K_{0.58}Na_{0.42}AlSi_3O_8$ ). Although the b and c cell parameters of this phase were found to remain essentially constant over the temperature range, a and  $\beta$  changed significantly. In order to explain these dimensional changes in terms of differential structural expansion, the high temperature structure of this feldspar was determined at 500°C and 1000°C. We found that the interatomic distances in the (Si,Al)-O framework remain constant with increasing temperature, whereas T-O-T, O-T-O and T-T-T angles undergo significant changes (T = Si,Al). These

observed changes can be explained by a flexing of the double-crankshaft chain of tetrahedra along the a axis.

We have also begun high temperature structural studies of another class of framework silicates which undergo little or negative axial expansion with temperature and are consequently of importance in ceramic materials designed to withstand moderate thermal shocks. Thermal expansion data for cordierite ( $\text{Mg}_2\text{Si}_5\text{Al}_4\text{O}_{18} \cdot \text{H}_2\text{O}$ ) and a Cs-rich beryl ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ) have been collected at temperatures up to 800°C. We are currently refining the structures of these two phases using intensity data collected at 400°C and 800°C in order to correlate axial and volume expansion with structural changes and to study the behavior of alkali cations and water molecules that reside in zeolitic channels in these structures.

The crystal structures of the  $\text{ThSiO}_4$  polymorphs thorite and huttonite were determined and refined in a study of the structural factors affecting susceptibility to radiation damage in minerals. This study is of interest because of the possible future storage of radioactive wastes in crustal rocks. Thorite commonly occurs in the metamict state whereas its polymorph huttonite does not. Although significant structural differences were found, no apparent cause of the different susceptibility to radiation damage was established. Continued work in this area is planned.

In collaboration with Dr. J. R. Clark of the U. S. Geological Survey, we are currently working out the room temperature atomic arrangement in the rare borate mineral hydrochlorborite ( $\text{Ca}_2\text{B}_8\text{O}_{15}\text{Cl}_2 \cdot 22\text{H}_2\text{O}$ ) using Patterson and direct methods. This mineral is novel because it occurs only during the driest seasons in playa lakes in China and Chile and dissolves when the ground water table approaches the surface.

## (2) Photoelectron Spectroscopy of Crystalline and Amorphous Silicates

Professional Associate: P. M. Fenn

We are continuing our study of electron binding energies in various crystalline and amorphous silicates in an attempt to detect

differences in Al, Si and O coordination environments. A number of crystalline and amorphous silicates have been examined using both Hewlett-Packard and Varian ESCA spectrometers. Our results to date indicate that coordination number differences between Al in various compounds are not detectable. We have observed shifts of up to 2 ev in the core level binding energies of Al, Si, and O between crystals and glasses of alkali feldspar compositions. Much smaller differences have been observed between  $\alpha$ -quartz and silica glass. Correlations between oxygen coordination, electronegativities of metal cations and the Si(2S) and O(1S) binding energies in a number of compounds have also been observed. Examination of other silica polymorphs as well as synthetic feldspar glasses is currently underway.

### (3) Semiempirical Molecular Orbital Calculations

Graduate Students: B.H.W.S. de Jong

B. G. Aitken

We have continued our study of the electronic factors affecting stability differences among molecular fragments representative of silicate structures. CNDO/2 calculations involving the molecules  $\text{Si}_2\text{O}$ ,  $\text{Al}_2\text{O}$ ,  $\text{H}_6\text{Si}_2\text{O}_7$ ,  $\text{NaH}_6\text{Si}_2\text{O}_7$  and  $\text{MgH}_6\text{Si}_2\text{O}_7$  in various geometric configurations have been carried out in an attempt to explain why Al-O-Al linkages are uncommon in stable silicate structures. We are also using this semi-empirical method to simulate valence band photoelectron spectra of quartz and silica glass.

### (4) Electrostatic and Repulsive Energies of Silicates

Professional Associate: P. M. Fenn

As part of our study of the factors affecting a mineral's stability, we have calculated the electrostatic energies of a number of silicates employing Bertaut's electrostatic energy summation procedure. Nearest-neighbor repulsive forces are estimated using bulk modulus data for simple oxides and fluorides. We have concentrated primarily on the potential energy differences among a number of structural models of the

intermediate alkali feldspar discussed in research report (1). Our results indicate that the alkali cavity has two distinct potential energy minima. A calculated energy difference of 12.6 kcal/mole exists between the structural model with the alkali atom occupying the center of its oxygen polyhedron and that with the alkali atom slightly off-center. The minimum energy, off-centered position corresponds to the position defined experimentally. In addition to these calculations, we have also studied the effect of Al/Si order-disorder in a variety of alkali feldspars on electrostatic energy differences.

(5) X-ray Radial Distribution Studies of Synthetic and Natural Silicate Glasses

Graduate Student: M. P. Taylor

Indirect information concerning the state of aggregation in silicate liquids may be obtained by studies of silicate glasses of various compositions. As part of a general, interdisciplinary study of the silicate melt and the genesis of magmatic crystals, we are continuing an investigation of structural variations in glasses from the system  $\text{NaAlSi}_3\text{O}_8(\text{Ab})-\text{KAlSi}_3\text{O}_8(\text{Or})-\text{SiO}_2(\text{Q})$ , utilizing radial distribution techniques. Data collection and reduction procedures have been developed over the past year. We are using a Picker Facs-I diffractometer operated in the step-scanning mode in steps of  $\sin 2\theta/\lambda$  for data collection on small diameter cylinders of solid glass. Radial distribution functions are calculated using the least-squares procedure of Konnert and Karl (1973, Acta Crystallog. A29, 702). Experimental RDF's have been determined for  $\text{NaAlSi}_3\text{O}_8$  and  $\text{KAlSi}_3\text{O}_8$  glasses and show several interesting features relative to the RDF for amorphous  $\text{SiO}_2$ . When Si-O, Si-Si, and O-O peaks are subtracted from the RDF of  $\text{NaAlSi}_3\text{O}_8$  glass, residual peaks occur at about 2.6 Å and 3.5 Å. We attribute these peaks to Na-O interactions. In addition to continuing these experimental studies, theoretical radial distribution functions have been calculated for various silicate structures using a quasi-crystalline model. Comparison of experimental and calculated RDF's for feldspar glasses suggests that they are similar to a tridymite-like

structure. Further work on glasses of other compositions is now in progress.

(6) Characterization of Two-Phase Mineral Intergrowths

Graduate Student: K. D. Keefer

Because of the potential information that intergrowths contain concerning the crystallization, subsolidus cooling history and alteration of rocks, we have begun a study of several types of mineral intergrowths including perthitic feldspars from volcanic and hypabyssal igneous rocks and pyroxene-amphibole intergrowths from eclogites. Perthites consist of intergrowths of Na- and K-rich feldspars on scales ranging from submicroscopic (cryptoperthites) to macroscopic (macroperthites). Because the intergrown phases differ in unit cell dimensions, they are commonly strained relative to the pure Na and K end-member feldspars.

We have successfully collected intensity data from the intimately intergrown Na- and K-rich phases of a cryptoperthite from volcanic rocks of Rabb County, New Mexico and are currently refining structural models for both phases in order to study structural differences between the intergrown phases and the pure end-member phases. Because of the small scale of the intergrowth, X-ray emission microanalysis of the intergrown phases yields only the bulk composition of the intergrowth. One of our primary goals in this study is to determine the individual compositions of the intergrown phases using the differences in X-ray scattering power between Na and K.

A second area of study now underway involves the origin and characterization of unusual intergrowths of amphiboles, pyroxenes and micas of possible mantle origin.

Reference Publications:

1. R. T. Dodd, J. E. Grover, and G. E. Brown, "Pyroxenes in the Shaw (L-7) chondrite," *Geochim. Cosmochim. Acta* 39, 1585-1594 (July, 1975).



2. G. E. Brown and P. M. Fenn, "High temperature structural study of an homogeneous, intermediate composition alkali feldspar," Prog. Geol. Soc. Amer. Ann. Mtg. 7, 1012 (November, 1975).
3. P. M. Fenn and G. E. Brown, "Energetics of the alkali site in K-Na feldspars," Prog. Geol. Soc. Amer. Ann. Mtg. 7, 1071-1072 (November, 1975).
4. B.H.W.S. de Jong and G. E. Brown, "Molecular orbital studies of (Si,Al)<sub>2</sub>O<sub>7</sub> groups in silicates," EOS, Trans. Amer. Geophys. Union 56, 1076-1077 (December, 1975).
5. M. P. Taylor and R. C. Ewing, "Crystal structures of the ThSiO<sub>4</sub> polymorphs, thorite and huttonite," EOS, Trans. Amer. Geophys. Union 56, 1076 (December, 1976).
6. P. M. Fenn, "The effect of pressure on the monoclinic alkali feldspar lattice," EOS, Trans. Amer. Geophys. Union 56, 1077 (December, 1976).
7. M. P. Taylor and G. E. Brown, "High temperature structural study of the P2<sub>1</sub>/a  $\rightleftharpoons$  A2/a phase transition in synthetic titanite, CaTiSiO<sub>4</sub>," Amer. Mineral. 61 (in press):
8. P. M. Fenn and G. E. Brown, "Crystal structure of a synthetic, compositionally intermediate hypersolvus alkali feldspar; evidence for Na/K site ordering. Zeit. Kristallogr. 142 (in press).

## 12. PHOTOELECTRONIC PROPERTIES OF SOLIDS

R. H. Bube, Professor, Materials Science and Engineering, and  
Electrical Engineering

### Professional Associates:

A. L. Fahrenbruch  
B. L. Mattes  
E. H. Z. Taheri

### Graduate Students:

J. Aranovich	J. W. McKenzie
F. Buch	K. W. Mitchell
S.-H. Chiao	H. A. Vander Plas
M. Chu	K. P. Vasudev
Y. Ma	
J. E. Mahan	

### Agency Support:

NSF-RANN	AER 75-16379
NSF	DMR 72-03-256-A01
ARO	DAHC04 73 C 0004
ARO	DAHC04 74 C 0025
NSF/MRL	through CMR

### Technical Objective:

To investigate the photoelectronic properties of solids, both crystalline and non-crystalline, in order to understand the underlying phenomena and to improve the properties and performance of electronically active materials and devices.

### Approach:

To couple a materials synthesis program closely to a utilization of a range of electrical conductivity, photoconductivity, luminescence, Hall and photo-Hall effect, thermoelectric and photo-thermoelectric effect, capacitance and photocapacitance, field effect, and optical measurement techniques, in order to investigate the properties of imperfections and structures involved in charge transport under the combined influence of optical excitation, thermal gradients, electrical and magnetic fields, and as a function of material composition.

Research Report:

(1) Applied Research on II-VI Compound Materials for Heterojunction Solar Cells

Graduate students: J. Aranovich  
F. Buch  
M. Chu  
K. Mitchell

p-CdTe/n-CdS, p-CdTe/n-ZnCdS, and p-CdTe/n-ZnSSe heterojunctions show promise to provide cells for solar energy conversion with maximum theoretical efficiency in the 17-23 percent range. One year ago we were making cells of p-CdTe/n-CdS with solar efficiency in the range of 3 to 4 percent. Our latest cells now show solar efficiencies in the range of 5.2 to 7.9 percent, the latter higher value still being with a cell with a known reflection loss of 6 percent. We have thus been moving steadily toward the value of 10 to 13 percent that these real cells should be capable of achieving. The improvement realized in the past year has been the result of our control of the vacuum evaporation or chemical spraying process for CdS films, the deposition of indium tin oxide (ITO) conducting layers as transparent front electrodes on the CdS films, and the application of partial anti-reflection coatings. By co-evaporation of indium, we can prepare CdS films by vacuum evaporation with excellent optical quality with controllable conductivity over the range from  $10^{-4}$  to  $500 \text{ (ohm-cm)}^{-1}$ . The ITO layer reduces the distributed series resistance loss, increasing the fill factor (ratio of maximum power delivered by the cell to the produce of short-circuit current and open-circuit voltage) from 0.55 to 0.66, and increasing the open-circuit voltage from 0.59 V to 0.63 V. The partial anti-reflection coating reduced reflection losses from 17 to 6 percent, thus increasing the short-circuit current.

Using electron-beam induced current techniques, the minority carrier length in the p-CdTe crystal substrate of the cell discussed above was measured to be  $0.4 \mu\text{m}$ . The existence of the high quantum efficiencies observed (approximately 0.75 averaged over the bandgap "window" - corrected for reflection) with such a small diffusion length implies a considerably larger optical absorption coefficient than

reported in the literature to date. This is a favorable result for all thin-film cells where the diffusion length is limited by grain size and most of the light must be absorbed within a diffusion length for useful collection.

Preliminary research on the heterojunction between ITO and p-CdTe has produced promising results. A large open-circuit voltage of 0.66 V and a small reverse saturation current have been observed. To date, however, fill factors are small and a large reverse bias is necessary to collect the current. The advantages of these cells would be their inherently large open-circuit voltage, large bandgap "window", and simplicity.

A number of heterojunctions were made by close-spaced vapor transport techniques, including p-CdTe/n-CdSe, p-CdTe/n-ZnSe, p-ZnTe/n-CdTe, and p-ZnTe/n-ZnSe. New values for the electron affinity of CdSe and ZnTe were determined with respect to that of CdTe. These junctions, as prepared, have a low quantum efficiency, the current transport being limited by insulating layers at the junction interface caused by interdiffusion at the high substrate temperatures used for this technique.

A p-CdTe/n-CdS solar cell made by solution-spraying a CdS film onto a single crystal p-CdTe substrate gave 5.6 percent solar efficiency (uncorrected for reflection loss), indicating promising properties for this mode of film deposition.

Supportive research is being carried out on properties of CdTe, as varied by annealing and ion implantation, together with the nature of electrical contacts to CdTe.

## (2) Electrical Transport in Amorphous Chalcogenide Semiconductors

Graduate students: J. E. Mahan  
H. A. Vander Plas

Field effect measurements on amorphous  $\text{As}_2\text{Te}_3$  and  $\text{As}_2\text{SeTe}_2$  show that field effect screening is controlled by mobile carriers at higher temperatures and by localized states at the Fermi level at lower temperatures. The mobile carrier density has a thermal

activation energy approximately the same as that of the electrical conductivity. Correlation with measurements of the temperature dependence of thermoelectric power shows that a two-band model involving conductivity both in extended states and in states lying above the valence edge provides the most consistent model for all of the data.

Concerning transport in  $\text{As}_2\text{Te}_3$ , the field effect investigation has revealed that (1) the conduction is strongly p-type with electron contribution to the conductivity less than about 0.01 of the hole contribution; (2) the conductivity mobility is apparently not thermally activated; (3) electron and hole densities are not greatly different, thereby implying that the ratio of electron to hole mobility is less than about 0.01; (4) a density of localized states of  $10^{19} \text{ cm}^{-3} \text{ eV}^{-1}$  at the Fermi level is observed. Quite similar results are obtained from field effect measurements on  $\text{As}_2\text{SeTe}_2$ .

Taken by themselves, the field effect measurements in the mobile carrier range could be interpreted in terms of a one-band model involving  $10^{18} \text{ cm}^{-3}$  mobile carriers with a mobility of  $10^{-4} \text{ cm}^2/\text{V-sec}$  in a band with effective density of states of  $10^{24} \text{ cm}^{-3}$ . To this field effect data, however, must be added input from the temperature dependence of thermoelectric power. A variety of different investigations indicate that the activation energy for conductivity is 0.14 eV larger than the activation energy for thermoelectric power in  $\text{As}_2\text{Te}_3$ . The most conventional interpretation has been that this 0.14 eV represents the activation energy of the carrier mobility; this is clearly in conflict with the field effect measurements described above. Another interpretation of the temperature dependence of thermoelectric power has been proposed: the apparent activation energy has no direct physical significance, but is generated by a transfer of conduction from one band (lying slightly above the extended states) to a second band (the extended states themselves) with increasing temperature. This two-band model can be used to fit both the temperature dependence of conductivity and thermoelectric power con-

sistently. Furthermore, the two-band model predicts much more reasonable quantitative values:  $10^{15} \text{ cm}^{-3}$  mobile carriers in extended states with mobility of  $10^{-1} \text{ cm}^2/\text{V-sec}$  and an effective density of states of  $10^{21} \text{ cm}^{-3}$ .

### (3) Photothermoelectric Effects in Semiconductors

Graduate students: Y. Ma  
H. A. Vander Plas

Measurements of thermoelectric and photothermoelectric power have been applied to three main areas of research: (1) properties of vacuum evaporated CdS films of suitable form for use in thin-film photovoltaic heterojunctions, (2) properties of solution-sprayed CdS films, and (3) properties of amorphous semiconductors prepared in sputtered thin-film form.

Thermoelectric power measurements were used to investigate the cause of the increase in electrical conductivity of CdS evaporated films as a consequence both of post-deposition annealing in  $\text{H}_2$  and of co-evaporation of indium donors. Heat-treatment in  $\text{H}_2$  after vacuum deposition increased the conductivity from  $10^{-4}$  to  $3 (\text{ohm-cm})^{-1}$ , the electron density from  $4 \times 10^{16}$  to  $6 \times 10^{18} \text{ cm}^{-3}$ , and the electron mobility from  $10^{-2}$  to  $3 \text{ cm}^2/\text{V-sec}$ . The increase in the electron mobility was accompanied by a decrease from 0.32 to 0.015 eV in the mobility activation energy. By co-evaporation of indium donors, values of electrical conductivity of  $115 (\text{ohm-cm})^{-1}$ , electron density of  $2 \times 10^{19} \text{ cm}^{-3}$ , and electron mobility of  $42 \text{ cm}^2/\text{V-sec}$ , were obtained. In both cases the increase in electron density due to the treatment reduces the effective intergrain barrier height by increasing the probability of tunneling through the barrier, and thereby increases the electron mobility in the film.

Both the structure and the electrical properties of solution-sprayed CdS films are found to vary markedly with substrate temperature, spraying rate, and cooling rate after spraying. The  $300^\circ\text{K}$  dark conductivity of the films deposited on glass exhibits maxima for substrate temperatures of about  $350^\circ$ ,  $400^\circ$  and  $450^\circ\text{C}$ . A  $20^\circ\text{C}$  differ-

ence in substrate temperature may correspond to two to three orders of magnitude difference in conductivity. The major contribution to these variations comes from comparable variations in mobility, with smaller variations in electron density; maximum conductivity corresponds primarily to maximum mobility, which corresponds in turn approximately to minimum intergrain barrier height. The effect of photoexcitation is to reduce differences caused by variations in substrate temperature, in a way consistent with considering photoexcitation as decreasing the barrier height and also enhancing tunneling through the barrier. Control of the properties of solution-sprayed CdS is a potentially significant consideration, since this process is probably the most inexpensive of the various methods of depositing CdS films for photovoltaic solar cell applications.

Results of thermoelectric power measurements on  $\text{As}_2\text{Te}_3$  amorphous films are described in section (2) above. In addition, further measurements have been made on amorphous  $\text{GeTe}_x\text{Te}_{1-x}$  materials, with ten values of  $x$  between 0.22 and 1.00. The Te-rich sample with  $x = 0.22$  is similar to V-VI materials like  $\text{As}_2\text{Te}_3$ , exhibiting one-carrier p-type conductivity with an apparent mobility activation energy of 0.18 eV. At the other extreme, for  $x = 0.75$  and  $x = 1.00$ , the materials are n-type over the entire range with an almost temperature-independent thermoelectric power. Two-carrier effects appear to dominate the intermediate compositions.

(4) Investigation of Deep Impurity Levels in GaAs by Photocapacitance and Related Techniques

Graduate students: S.-H. Chiao  
K. P. Vasudev

Relatively low concentrations of unknown residual deep impurities in GaAs limit the frequency response, noise level and efficiency of a variety of GaAs devices. Photocapacitance and related techniques like thermally stimulated capacitance are ideal additions to standard photoelectronic techniques for investigating the deep levels because of their high resolution, their sensitivity, and their ability

to interact with both radiative and non-radiative imperfections. We have been investigating (1) liquid-phase epitaxial (LPE) layers of GaAs, (2) bulk GaAs:Cr substrate material, (3) bulk GaAs:O substrate material, (4) GaAs:Cu LPE layers with Cu introduced during growth, and (5) GaAs:Cu LPE layers with Cu introduced by diffusion after growth.

In LPE GaAs grown without doping an acceptor-like trap level at 0.4 eV above the valence band appears to be very important in controlling the compensation between shallow donors and acceptors. This level could be associated with a complex native defect such as  $(\text{Si}_{\text{Ga}} \text{V}_{\text{As}})^{-}$  or it could be more than coincidence that Cu has a level at the same position in the gap. In addition to this level, there are several other defects of lesser concentration at 0.75, 0.93 and 1.42 eV. The 0.75 eV level appears similar to an oxygen level measured separately on an oxygen-doped sample, and its concentration fluctuates with the growth system parameters.

For LPE material grown on semi-insulating Cr-doped substrates, there is an out-diffusion of Cr and perhaps other impurities from the substrate, which cause the interface to be high resistivity and reduce the effective thickness of the epitaxial layer.

Cu introduced into the growth of LPE GaAs increases the n-type conductivity; Cu diffused into grown LPE GaAs acts as a conventional acceptor with level about 0.45 eV above the valence band. The photo-electronic properties of Cu-diffused LPE GaAs have been carefully explored using measurements of dark conductivity and Hall effect vs T, photoconductivity and photo-Hall effect vs T, spectral response of photoconductivity, thermally stimulated conductivity, and optical quenching of photoconductivity. Results are in general good agreement with previous investigations of Cu impurity in bulk GaAs.

In addition to locating the energy levels, all the significant trap parameters (thermal and optical cross sections, concentrations) have been determined for Cr and O - the two most important deep levels in GaAs.



Based on the growth system parameters and the capacitance measurements on LPE GaAs, a thermodynamic model for the incorporation of the main residual impurities (Si, O, C) has been developed.

Reference Publications:

1. G. H. Blount, M. K. Preis, R. T. Yamada and R.H.Bube, "Photoconductive Properties of Chemically Deposited PbS with Dielectric Overcoatings," J.Appl.Phys. 46, 3489 (1975)
2. R. H. Bube, "Electronic Transport in Polycrystalline Films," Annual Review of Materials Science 5, 201 (1975)
3. A. L. Fahrenbruch, F. Buch, K. Mitchell and R. H. Bube, "II-VI Photovoltaic Heterojunctions for Solar Energy Conversion," 11th IEEE Photovoltaic Specialists Conference, p. 450 (1975)
4. R. H. Bube, "Photoconductivity of Amorphous Semiconductors," RCA Rev. 36, 467 (1975)
5. R. H. Bube, "The Effect of Defects on the Photoconductivity of Solids," J.Electron.Mat. 4, 991 (1975)
6. A. L. Lin and R. H. Bube, "Effects of Heat Treatment and Plastic Deformation on the Photoelectronic Properties of High-Resistivity GaAs:Cr," J.Appl.Phys. 46, 5302 (1975)
7. C. J. Park, J. E. Mahan, R. T.-S. Shiah, H. A. Vander Plas, and R. H. Bube, "Electronic Transport in Amorphous Germanium Arsenides," J.Appl.Phys. 46, 5307 (1975)
8. A. L. Lin, E. Omelianovski, and R. H. Bube, "Photoelectronic Properties of High-Resistivity GaAs:O," accepted for J.Appl.Phys., May (1976)
9. A. L. Lin and R. H. Bube, "Photoelectronic Properties of High-Resistivity GaAs:Cr," accepted for J.Appl.Phys., May (1976)
10. R. T.-S. Shiah and R. H. Bube, "Photoconductivity of Amorphous Compound Semiconductors Involving Elements from Groups IV, V, and VI," accepted for J.Appl.Phys., May (1976)
11. J. L. Crowley, R. A. Wallace and R. H. Bube, "Ionic Transport in Sulfonated Polystyrene Polyethylene Polyelectrolyte," accepted for J.Polymer Science
12. R. H. Bube, "How Many Data Establish A Model? Electrical Transport in Amorphous As<sub>2</sub>Te<sub>3</sub> and Polycrystalline PbS," accepted for J.Appl.Phys., May (1976)
13. P. K. Vasudev, B. L. Mattes, E. Pietras, and R. H. Bube, "Excess Capacitance and Non-Ideal Schottky Barriers on GaAs," accepted for Solid-State Electronics

14. F. Buch, A. L. Fahrenbruch and R. H. Bube, "Photovoltaic Properties of n-CdSe/p-ZnTe Heterojunctions," accepted for Appl.Phys.Lett. May 15, 1976
15. R. H. Bube, "Non-Conventional Heterojunctions for Solar Energy Conversion" in Critical Materials Problems in Energy Production, C. Stein, ed., Academic Press (1976)

### 13. X-RAY EXCITATION OF SUPERATMOSPHERIC LASERS

R.L. Byer, Associate Professor, Applied Physics

#### Professional Associates

R.L. Herbst

#### Graduate Students

M.M. Choy\*  
R.N. Fleming\*  
M.A. Hennesian  
H. Komine  
S. Warshaw\*\*

J.I. Levatter  
S.J. Brosnan  
D.C. Wolfe  
R.A. Baumgartner

\*Received PhD during report period.

\*\*Received Engineers Degree during report period.

#### Agency Support

LASL XP4 51377  
SRI 13851  
Honeywell 73-CR-009  
F44620-74-C-0039  
ERDA E(29-2)3570  
EPRI RP 486-1  
N00014-75-C-0894  
DAHC 04-74-C-0033  
NSF/MRL through CMR

#### Technical Objective

To design and analyze a scalable high pressure gas laser system using X-ray preionization followed by a controlled mode glow discharge pumping.

#### Approach

The use of electron beams and ultraviolet photons for preionization of high pressure discharges is well known. However, these methods suffer from lack of scalability to high pressures due to the limited 10 atm-cm penetration depth in gases. In addition, the electron beam excitation process involves the use of a thin (.005") metal foil window which suffers thermal heating and stress during excitation, thus limiting the repetition rate to near 1 pps.

We have proposed and analyzed<sup>1</sup> using X-ray radiation for pre-ionization of high pressure gas discharges. The X-rays penetrate in a controlled manner and allow device scaling to tens of atmospheres over tens of centimeters diameters. In addition, the X-ray pre-ionization method solves the thermal loading foil window problem. Our initial design laser with dimensions of 2 cm diameter by 30 cm in length should allow 300 J output energy per pulse at 10.6  $\mu$ m of a CO<sub>2</sub> : He : N<sub>2</sub> mixture at 10 atm pressure. Operating at 20% efficiency the device should be able to run at 1000 pps and thus generate 300 kW of average power without thermal problems.

---

<sup>1</sup>J.I. Levatter and R.L. Byer, "X-Ray Excited Superatmospheric Laser", presented at the Nuclear Pumped Laser Workshop, Monterey, California, April, 1976.

#### Reference Publications

1. M.M. Choy, S. Ciraci and Robert L. Byer, "Bond Orbital Model for Second Order Susceptibilities", IEEE Journ. of Quant. Electronics, vol. QE-11, No. 1. (January 1975).
2. R.L. Byer, "Nonlinear Optical Phenomena in Oxides and Application to a Tunable Coherent Spectrometer", Journ. of Solid State Chemistry, 12, p.156, (March 1975).
3. R.L. Byer, "Remote Air Pollution Measurement", reprinted from Proc. ICO Conf. on Opt. Methods in Sci. and Indust. Measure. Tokyo, 1974. Japan J. Appl. Phys. 14, Suppl. 14-1, (1975), see also Optical and Quantum Electronics, 7, p.147-177, (1975).
4. H. Komine and R.L. Byer, "Proposed Atomic Mercury Anti-Stokes Frequency Converter", Appl. Phys. Letts. vol. 27, No. 5, (September 1975).
5. R.L. Byer, R.L. Herbst, R.N. Fleming, "A Broadly Tunable IR Source", Lecture Notes in Physics, Laser Spectroscopy, (43), ed. S. Haroche, J.C. Pebay-Peyroula, T.W. Hansch and S.E. Harris, Springer-Verlag, Berlin, Heidelberg, New York, p.207, (November, 1974).

6. M.A. Henesian, R.L. Herbst and R.L. Byer, "Optically Pumped Superfluorescent Na<sub>2</sub> Molecular Laser", Journ. of Appl. Phys. vol. 47, No.4, p.1515, (April 1976).
7. R.L. Byer, "Initial Experiments with a Laser Driven Stirling Engine", published in Second NASA Conference on Laser Energy Conversion, proc. of Conf. held at NASA/Ames Research Center, Moffett Field, California, January 27-28, 1975.

14. STUDIES IN HOMOGENEOUS CATALYSIS AND THE SYNTHESIS OF  
METAL-METAL BONDS

James P. Collman, Professor of Chemistry

Professional Associates:

C. M. Elliott  
S. E. Hayes  
B. Kuznetsov  
E. P. Rose

F. M. Rose  
G. Schmuckler  
B. S. Tovroy

Graduate Students:

P. A. Christian  
P. Denisevich  
R. G. Finke  
S. E. Groh  
T. R. Halbert  
A. Madonik  
M. L. Marrocco  
P. L. Matlock

R. K. Rothrock  
M. K. Neuberg  
E. R. Schmittou  
T. N. Sorrell  
R. A. Stark\*  
K. Suslick  
R. Walker

Agency Support:

NSF MPS75-17018  
ARPA through CMR, N00014-75-C-1171  
NIH GM17880  
NSF GP39451

\*Received Ph.D. during report period.

### Technical Objectives:

This research has as its long range goals the development of homogeneous and hybrid homogeneous-heterogeneous catalysts for liquid phase oxidation and reduction reactions and for electrode catalysis. Future emphasis will also be given to soluble clusters of transition metal atoms.

### Approach:

We are synthesizing transition metal porphyrin complexes which mimic the active sites in the oxygen carriers--hemoglobin and myoglobin--and in the oxygenases, cytochrome P-450. We are also preparing "face-to-face" binary porphyrins which are intended to serve as electrode catalysts for the oxygen cathode of a fuel cell and for electrolytic fixation of nitrogen and carbon monoxide. We are attempting to devise general methods for the synthesis of coordinatively unsaturated transition metal clusters and to explore their use as homogeneous catalysts. We are also developing organotransition reagents for stoichiometric organic synthesis and we are exploring their reaction mechanisms.

### Attempted Synthesis of One-Dimensional Intermetallic Polymers

For the past several years we have been attempting the preparation of linear polymers whose backbone is comprised entirely of metals or heavy elements. Our interest in such materials stems from the expectation that a coaxially oriented solid derived from such substances might exhibit anisotropic electron transport properties which would be principally dependent upon the structure of the individual polymer molecules. This work was being carried out as a part of a long standing collaboration

with Professor W. A. Little, Physics, in a program directed towards examining the feasibility of Little's hypothetical excitonic superconductor.

We have recently decided to abandon synthetic efforts in this field in view of our finding that the germanium sulfur or germanium selenium bonds<sup>1</sup> we were using to prepare such polymers are unstable towards hydrolysis or solvolysis under very mild conditions. We have also been frustrated in our search for general methods of preparing germanium disulfides and thiols.

#### Models for Mixed-Function Oxygenases

During the past year we have extended and clarified our earlier work characterizing the coordination spheres in the recognized stages of the oxygenase cytochrome P-450<sup>2-8</sup>. Using esr, electronic spectra, MCD spectra, Mössbauer spectra, and X-ray crystallography, we have been able to establish that mercaptide is an axial base which is bound to two of the ferric and to the ferrous carbonyl stages of the enzyme. This work has led to the synthesis of new "picket fence porphyrins" with appended axial bases.

#### The Preparation of Catalytic Electrodes

This new project is partially derived from our studies of oxygen binding iron porphyrins and catalysts bound to solid-state supports. We are attempting to prepare "face-to-face" binary porphyrin complexes which should rapidly reduce molecular oxygen in the inter-porphyrin cavity. We plan to attach members of this new class of porphyrins to conducting surfaces affording catalytic oxygen cathodes for ultimate use in fuel cells. This project is part of a large joint effort involving Boudart (Chem. Engineering), Taube (Chemistry), Anson



(Chemistry, California Institute of Technology) and Tennent (Hercules Corp.). We have now prepared two well-characterized "face-to-face" porphyrins and have begun to characterize the physical properties of the porphyrins. ESR spectra and electrochemical techniques have been used to demonstrate direct interaction between the two metals in one of these systems. We have initiated studies designed to bind simple and "face-to-face" porphyrins to graphite surfaces and to explore their electrochemical behavior. This work is making use of a new electrochemical technique developed by Anson at Caltech and during the next year we shall employ high porous conducting graphites provided by the Hercules group.

#### Iron Carbonyl Reagents for Organic Synthesis

Our studies on the mechanism of disodium tetracarbonylferrate<sup>9</sup> and of the binary complex,  $\text{Na}_2\text{Fe}_2\text{CO}_8$ , have been thoroughly completed in collaboration with Brauman (Chemistry). This work is being written up. The latter compound provides the first case of a mechanism by which a binary metal complex carries out an organic transformation and contrasts the behavior of mononuclear and binuclear metal compounds.

#### Transition Metal Clusters and Fischer-Tropsch Catalysis

We have initiated a program designed to synthesize coordinatively unsaturated transition metal clusters and to mimic stages of the heterogeneous Fischer-Tropsch system with homogeneous complexes involving two or more metal atoms. This work is in an embryonic stage, but will be expanded during the next year.

## Publications:

1. J. P. Collman, P. A. Christian, S. Current, P. Denisevich, T. R. Halbert, E. R. Schmittou, and K. O. Hodgson, "The Molecular Structure of transMethyliodo{difluoro[3,3' - (trimethylene dinitrillo)-di-2-pentanone dioximate]}borate} rhodium(III)", *Inorg. Chem.* 15, 223 (1976).
2. J. P. Collman, R. Gagne, J. Kouba, and H. Ljusberg-Wahren, "Reversible Oxygen Adduct Formation in Co(II) 'Picket Fence' Porphyrins", *J. Amer. Chem. Soc.*, 96, 6800 (1974).
3. J. P. Collman, T. Sorrell, and B. Hoffman, "Models for Cytochrome P-450", *J. Amer. Chem. Soc.* 97, 913 (1975).
4. J. P. Collman, R. Gagne, C. Reed, T. Halbert, G. Lang, and W. Robinson, "Picket Fence Porphyrins--Synthetic Models for Oxygen Binding Hemoproteins", *J. Amer. Chem. Soc.* 97, 1427 (1975).
5. J. P. Collman, J. L. Hoard, N. Kim, G. Lang, and C. A. Reed, "The Synthesis, Stereochemistry, and Structure-Related Properties of  $\alpha,\beta,\gamma,\delta$  -Tetraphenylporphinatoiron(II)", *J. Amer. Chem. Soc.* 97, 2676 (1975).
6. J. P. Collman and T. Sorrell, "A Model for the Carbonyl Adduct of Ferrous Cytochrome P-450", *J. Amer. Chem. Soc.* 97, 4133 (1975).
7. J. P. Collman, J. I. Brauman, and K. S. Suslick, "Oxygen Binding to Iron Polphyrins", *J. Amer. Chem. Soc.* 97, 7185 (1975).
8. J. P. Collman, T. N. Sorrell, J. H. Dawson, J. R. Trudell, E. Bunnenberg, and C. Djerassi, "Magnetic Circular Dichroism of the Ferrous Carbonyl Adducts of Cytochrome P-450 and P-420 and their Synthetic Models; Further Evidence for Mercaptide as the Fifth Ligand to Iron", *Proc. Nat. Acad. Sci. U.S.* 3, 6 (1976).
9. J. P. Collman, "Disodium Tetracarbonylferrate--A Transition Metal Analogue of Grignard's Reagent", *Accounts Chem. Res.* 8, 342 (1975).

## 15. INTERACTIONS OF SOLIDS WITH SOLUTIONS

F. W. Dickson, Professor of Geochemistry, Geology Department

### Professional Associates:

J. L. Bischoff  
A. S. Radtke  
J. D. Vine  
L. Price  
M. J. Mottl

### Graduate Students:

W. E. Dibble	J. L. Renner
J. L. Krumhansl	J. J. Rytuba
J. A. Peterson**	

\*\*Received MSc during report period.

### Technical Objectives:

The interaction of aqueous solutions with rocks and minerals is being studied at temperatures from 25°-200°C and 1-2000 bars by use of gold-cell hydrothermal solution equipment. The equilibrium and kinetic behaviour of chemical systems relevant to understanding geochemical processes is determined. Some studies of metallic sulfide equilibria and sulfur isotopes are being done to clarify subsidiary questions.

### Research Report:

Work was completed on the phase relations in the system  $\text{Ti}_2\text{S}-\text{As}_2\text{S}_3$  from 200°-450°C. This study was part of the M. Sci. Thesis of J. A. Peterson. The major work accomplished this year was on the study of the interaction of aqueous solutions and rocks of basaltic and granitic compositions. Work on the interaction of basalt and seawater at various temperatures and pressures was done jointly with Dr. Bischoff of the U.S. Geological Survey. These studies are continuing with the support of the National Science Foundation. Results of this work were presented at the Fall Annual Meeting of the American Geophysical Union. Studies of the interaction of seawater with

granitic rocks at high temperatures and pressures were undertaken and are continuing with the cooperation and support of the Dept. of Scientific and Industrial Research in New Zealand. Studies of the reaction of granite with dilute aqueous solutions continued as part of the Lithium Project of the U.S.G.S. directed by Dr. Vine. This work is being done in liaison with the Stanford Geothermal Program in the Schools of Earth Science and of Engineering. Results of this work were presented at a symposium on lithium sponsored by the U.S.G.S., and a portion has been submitted for publication. Studies of the interaction of water and hydrocarbon-bearing rocks, as well as the interaction of water and petroleum as a function of temperature and pressure, continued in liaison with Dr. Price of the U.S.G.S. Sulfur isotope studies are also in progress.

#### Reference Publications:

1. W. E. Dibble, Jr. and F. W. Dickson, 1976, "The behavior of lithium in experimental rock-water interaction studies, U.S. Geological Survey Prof. Paper (in press).
2. F. W. Dickson, A. S. Radtke, and R. O. Rye, 1975, Implications of the occurrence of barium minerals and sulfur isotopic compositions of barite on late-stage processes in Carlin-type gold deposits (Abs.): Abstracts with Program, 1975, Rocky Mountain Section, Ann. Meeting, v. 7, no. 5, p. 604, Geol. Soc. America, Boise, Idaho.
3. A. S. Radtke, F. W. Dickson, and J. Rytuba, 1974, Genesis of disseminated gold deposits of the Carlin type: Abstracts with Program 1974 Cordilleran Section, Annual Meeting, Geological Society of America, Las Vegas, Nevada, p. 239-240.
4. A. S. Radtke, C. M. Taylor, F. W. Dickson, and Chris Heropoulos, 1974, Thallium-bearing orpiment, Carlin gold deposit, Nevada: Jour. Research, U.S. Geol. Survey, v. 2, no. 2, p. 341-342.
5. A. S. Radtke, C. M. Taylor, R. C. Erd, and F. W. Dickson, 1974, Occurrence of lorandite,  $\text{TlAsS}_2$ , at the Carlin gold deposit, Nevada: Econ. Geology, v. 68, no. 1, p. 121-123.

6. A. S. Radtke and F. W. Dickson, 1975, Carlinite,  $Tl_2S$ , a new mineral from Nevada: Am. Mineralogist, v. 60, nos. 7 and 8, p. 559-565.
7. A. S. Radtke and F. W. Dickson, 1976, Genesis of Carlin-type gold deposits in the framework of tectonic evolution of the Basin and Range province (Abs.): Soc. Mining Engineers, Am. Inst. Mining, Metall. Petroleum Engineers, Ann. Mtg., Las Vegas, Nevada, Mining Engineering, v. 27, no. 12, December 1975, p. 69.
8. A. S. Radtke and F. W. Dickson, 1976, Structural controls and genesis of Carlin-type gold deposits in the evolution of the Basin and Range province: Am. Inst. Mining, Metall. Petrol. Engineers, Ann. Meeting, Las Vegas, Nevada. Preprint no. 75-I-39, 8 p.
9. A. S. Radtke and F. W. Dickson, 1976, General features of disseminated replacement gold deposits of the Carlin type: Symposium on Disseminated Gold Deposits, Mackay School of Mines, Reno, Nevada, March 26-27, 1976, Preprint with program, 3 p.
10. W. E. Seyfried, Jr., J. L. Bischoff, and F. W. Dickson, 1975, Basalt-seawater interactions from 25°C-300°C and from 1-500 bars: an experimental study, EOS Trans., Am. Geophysical Union, V. 56, no. 12, p. 1073.

16. METHODS OF QUANTUM FIELD THEORY APPLIED TO COOPERATIVE PHENOMENA PROBLEMS

S. Doniach, Professor of Applied Physics

Professional Associates:

R.A. Klemm  
J. Zittartz

Graduate Students:

J.N. Fields  
D.M. Lublin  
D.K. Misemer  
E. Rezayi  
L. Turkevich  
D. Jackson

Agency Support:

Army AROD  
NSF/MRL through CMR  
NSF Biology

Technical Objective:

To apply the methods of quantum field theory to understanding excitations and cooperative phenomena occurring in a variety of materials.

Research Report:

(1) Cooperative Phenomena in Lipid Bilayers (membranes)

Work has been started on a study of the theory of phase transitions in phospholipid bilayers. A mapping of the general statistical mechanical problem involved has been developed onto a simple Ising model. This model allows for study of weakly first order phase transitions in the complex situation of mixtures of different molecules which occur in biological membranes. An extension of a three component Ising model (due to Blume, Emery and Griffiths) is being developed to exploit an analogy between  $\text{He}^3$  -  $\text{He}^4$  mixtures and mixtures of phospholipids with cholesterol.

Work is being started to study the processes of transport of Ca ions through lipid vesicles using x-ray absorption spectroscopy at the synchrotron lab.

## (2) Theory of the Magnetic State of Mixed Valence Compounds

These compounds such as  $\text{SmS}$  and  $\text{PuAl}_2$  show strong evidence that the f-electrons are partly in a localized state and partly in a conduction band (d-band). One mystery in this subject is the fact that although the f shell shows an odd number of electrons for part of the time it does not appear to exhibit a magnetic moment. A new theory is being developed in which the f spins have their moments quenched by the conduction electrons in a condensed Kondo state. As the parameters of the system vary this Kondo type paramagnet could become an antiferromagnet at low temperatures. Work is being pursued in the theory of a one-dimensional system of localized spins coupled to a one-dimensional electron gas. It appears possible to map this problem onto the problem of backscattering in a 1-dimensional electron gas previously studied by field theory techniques. This will allow a rigorous evaluation of the boundaries in the phase diagram for this artificial one-dimensional system and can give a good mathematical foundation to ideas about what happens in real materials in 3 dimensions. The work is being done with Joe Fields.

## (3) Critical Fields in Highly Anisotropic Superconducting Systems

Recent work on  $(\text{SN})_x$  suggests that these are quasi one-dimensional superconductors. Lee Turkevich has been expanding the usual theory of vortex formation in high fields using the Ginzburg-Landau formalism to a system of coupled one-dimensional chains. He finds that the critical field ( $H_{c2}$ ) is a strong function of angle in the plane perpendicular to the chain direction. This calculation can also be extended to calculate the critical field of weakly coupled bundles of chains — a coupled Josephson system. It appears that real  $(\text{SN})_x$  samples would be composed of such bundles.

## (4) Theory of Coupled Chains of Strongly Interacting Electrons

Dick Klemm has been working in collaboration with P. Lee and M. Rice of Bell Labs on a theory of chains coupled in pairs such as occur in the

compound TTF-TCNQ. The phase diagram for possible superconducting and charge density wave transitions for such a system of a pair of chains has been worked out in detail. This work is being submitted for publication.

(5) Theory of Fluctuations in the XY Model

J. Zittartz (on leave from the University of Köln, Germany) has worked out a theory of fluctuations in the XY model. This theory, which neglects the effects of vortices, suggests a new type of phase transition phenomenon for such a two-dimensional system. The work has been published in Zeitschrift für Physik.

(6) Theory of the Peierls Charge Density Wave Transition in a One-Dimensional Electron Gas

Ed Rezayi has been studying the theory of a strongly coupled electron gas (Luttinger model) extended to include the electron phonon coupling to all orders. He finds that the response functions of this system exhibit a new kind of singularity as the temperature is lowered towards absolute zero. The formation of a charge density wave appears in this calculation to be accompanied by zero frequency charged density wave order parameter fluctuations. This could explain experiments on neutron scattering from potassium tetracyano-platinate (KCP) which to date have not been explainable in mathematical terms.

(7) Calculation of X-ray Absorption Cross Sections for a Variety of Atoms

Dave Misemer is calculating the dipole matrix elements for L-shell x-ray absorption in a variety of atoms. This calculation uses Hartree Fock programs previously developed by Brian Kincaid. The resulting calculations will be used to analyze data taken by Spicer, Lindau and collaborators on photoabsorption in the 100 to 600 eV range at the synchrotron lab.



### Publications

- S. Doniach, in Proceedings of Summer School on Photoionization and related phenomena, Plenum Press, 1976 (ed. F. Wuillemier)
- R.A. Klemm and H. Gutfreund, Phys. Rev. 1976.
- J. Zittartz, Z. f. Physik, B23, 55,63 (1976).
- D. Lublin, Phys. Rev. Letters, 34, 568 (1975).

17. COAL SLAG PHENOMENA IN OPEN CYCLE MHD GENERATORS

R. H. Eustis, Professor, Mechanical Engineering and Director,  
High Temperature Gasdynamics Laboratory

Professional Associates:

C. H. Kruger, Professor, Mechanical Engineering  
S. A. Self, Adjunct Professor  
J. K. Koester, Senior Research Associate

Graduate Students:

P. C. Ariessohn\*\*  
M. K. Jenkins\*\*

R. M. Nelson  
M. E. Rodgers

\*\*Received MS during report period.

Agency Support:

EPRI RP468-1

Technical Objective:

The technical objective of this research program is to provide an understanding of the effect on performance of magnetohydrodynamic (MHD) generators of coal slag deposits on the channel walls. These deposits are expected to influence the fluid mechanics, electrical performance, and materials selections for MHD generators.

Approach:

The program involves studies of the fluid mechanics of slag layers including the mechanism of deposition, the effect of slag droplets and mineral vapor on plasma conductivity, and the effect of slag layers on the electrical performance of MHD generators. A special effort is made to incorporate extensive diagnostics into the experimental program for direct measurement of as many parameters as possible. The laboratory program is accompanied by a modeling effort which is useful both in understanding the physical processes which occur and in extrapolating results to other conditions or to larger scale systems.

Extensive analyses of the coal slag deposits on the walls and of slag-wall material interface are an important part of this investigation.

**Publications:**

1. J. K. Koester and R. H. Eustis, "In-Channel Observations on Coal Slag", Workshop on Replenishment in MHD-Generators, National Bureau of Standards, December 17, 1975, proceedings to be published.
2. J. K. Koester, M. E. Rodgers, and R. H. Eustis, "In-Channel Observations on Coal Slag", 15th Symposium Engineering Aspects of Magnetohydrodynamics, May 24-26, 1976, The University of Pennsylvania.

18. EXPERIMENTS AT LIQUID HELIUM TEMPERATURES ON MACROSCOPIC QUANTUM EFFECTS,  
MATERIAL PROPERTIES, GENERAL RELATIVITY, AND SUPERCONDUCTING ACCELERATORS

W. M. Fairbank, Professor of Physics  
C. W. F. Everitt, Adjunct Professor  
R. P. Giffard, Assistant Professor of Physics  
H. A. Schwettman, Professor of Physics

Professional Associates:

J. T. Anderson	J. M. Madey
S. P. Boughn	J. Malmivuo
D. P. Boyd	M. S. McAshan
B. Cabrera	H. J. Paik
P. H. Ceperley	T. I. Smith
L. R. Elias	J. P. Turneure
G. C. Li	F. van Kann
J. A. Lipa	J. P. Wikswo, Jr.
J. M. Lockhart	F. C. Witteborn
C. M. Lyneis	P. W. Worden, Jr.

Graduate Students:

S. P. Boughn*	J. S. Philo
D. E. Claridge*	R. A. Sears
D. A. Deacon	M. A. Taber
J. N. Hollenhorst	A. M. Vetter, Jr.
G. S. LaRue	C. A. Waters
J. M. Lockhart*	J. P. Wikswo, Jr.*
P. L. Marston*	G. A. Westenskow
P. F. Michelson	E. G. Wilson*
B. J. Neuhauser	P. W. Worden, Jr.*
T. P. Orlando	

\*Received Ph.D. during Report Period

Agency Support:

AFOSR F44620-75-C-0070  
AFOSR F44620-75-C-0022  
NASA NGR-05-020-019  
N00014-75-C-0786  
NSF MPS73-08748-A02  
NSF MPS73-08836-A02  
NSF DMR75-15628 and NSF DMR75-15628-A01  
NSF MPS73-08870-A03  
NSF APR72-03447-A03  
AFOSR76-2913

### Technical Objective:

This research is directed toward the study of the basic problems of physics using low temperature techniques. In addition to experiments studying the special properties of superconductors and helium for their sake, we exploit their unique properties to perform experiments in other fields of physics such as gravitation and relativity, biophysics and medicine, particle accelerators and the search for fractionally charged particles.

### Research Report:

#### (1) Positron Source

Senior Research Associate: J. M. Madey

A source of magnetic ground state positrons at energies below  $10^{-7}$  eV is required for operation of the positron free fall experiment. Positrons in this energy range cannot be obtained from natural  $\beta^+$  emitters.

The approach we have adopted is to capture a small number of relatively low energy ( $\sim 100$  eV) positrons and to trap them within a solenoidal magnetic field between electrostatic mirrors. Provided that the trap proves to be stable, the positrons can readily be thermalized to energies of the order of  $10^{-4}$  eV. Adiabatic expansion can be used to lower the energy to the required  $10^{-7}$  eV.

#### (2) Photon Counting Detector

Senior Research Associate: J. M. Madey

We are developing a photo-electric effect detector for use at millimeter wavelengths. The detector is based on excitation of the  $n = 1$  cyclotron level of magnetic ground state electrons trapped in a high Q cavity resonant at the cyclotron frequency. Theoretical estimates of the performance predict a noise temperature less than  $1^\circ\text{K}$  and quantum efficiencies of the order of 10%. Such a detector would have immediate application in millimeter wave radio astronomy.

(3) Force of Gravity on Elementary Charged Particles and Surface Shielding Effect

Postdoctoral Fellow: J. M. Lockhart

Visiting Scholar: F. C. Witteborn

Low energy electron beam techniques have been developed which permit the measurement of the force of gravity on single electrons and positrons, thus allowing a direct test of the gravitational equivalence of matter and anti-matter. The electron experiment has already been performed, yielding results which seem clear, but which also seem to indicate the presence of an unexplained shielding effect in the metallic drift tubes used in the experiment. Recent work has been directed toward exploring the nature of this shielding effect and the conditions under which it exists. There appears to be strong evidence for the presence of a large temperature dependence in the magnitude of the shielding. Experiments are now in progress to determine the detailed behavior of this temperature dependence. Measurements on the positron await the completion of a source of ultra-low energy positrons; a prototype of this source should be ready for tests in the next few months.

(4) Free Electron Laser

Senior Research Associate: J. M. Madey

Research Associates: L. Elias

T. Smith

Theory indicates the possibility of amplification due to stimulated emission of magnetic bremsstrahlung (synchrotron radiation) by free electrons in a spatially periodic magnetic field. Experimentally, we have used a 24 MeV electron beam to amplify 10  $\mu$  infrared radiation and have established a lower bound to the optical power density for saturation. We are now preparing to operate a free electron laser oscillator.

(5) Magnetic Susceptibility of Biological Molecules

Graduate Student: J. S. Philo

We have developed a new type of magnetic susceptibility apparatus using a superconducting magnet and a Josephson junction magnetometer. At present we have achieved a sensitivity of  $10^{-6}$  of the diamagnetic

susceptibility of water. This high sensitivity should allow us to measure the small changes in molecular diamagnetism which occur during such processes as the unwinding of DNA helices, conformation changes in proteins, phase transitions in membranes, etc. In addition to high sensitivity, the instrument has a response time of a millisecond, which allows us to study the kinetics of hemoglobin reacting with carbon monoxide and other fast reactions in solutions.

(6) Development of a Sensitive Cryogenic Gravitational Wave Detector

Postdoctoral Fellows: S. P. Boughn  
H. J. Paik

We have designed and constructed a 1400 pound cryogenic gravitational wave detector. The antenna, which is a cylindrical aluminum bar, is covered with niobium-titanium and has been levitated on a 2 kilogauss magnetic field. The source of this field is a set of five, single layer, "pancake-type" coils which are strung in series and operated in a persistent mode. This levitation scheme provides both uniform support for the detector and acoustic isolation for the detecting system. To sense vibrations in the antenna we are developing a superconducting tunable-diaphragm transducer for the low temperature gravitational wave detector. The transducer consists of a thin circular niobium diaphragm clamped around the edge. Two niobium-titanium pancake coils are located close to the two surfaces of the diaphragm and a third coil coupled to a SQUID is connected in parallel with the two pancake coils. A large dc current is stored in the superconducting loop formed by the pancake coils. When this transducer is attached to the end of the gravitational wave antenna and tuned by means of the dc current to the resonant frequency of the antenna under observation, the diaphragm picks up the motion of the bar, amplifies it by the square root of the mass ratio and converts it into electromagnetic signals in the coils by means of inductance modulation. The ac magnetic field generated in the third coil is detected by an extremely low noise superconducting magnetometer. When operating, this detector will be the first instrument sensitive enough to detect predicted gravitational radiation of known astrophysical events in our galaxy. We expect eventually to achieve  $10^6$  improvement in energy sensitivity over Weber's for our 3m°K gravitational wave detector.

(7) Optical Measurement of Surface Profile of Rotating Liquid Helium

Graduate Student: P. L. Marston

We are examining the surface contour of He II in a rotating "bucket" to attempt to observe the vortex array and other superfluid effects. Coherent optical techniques are employed including the observation of the diffraction pattern, phase contrast image, and Fizeau fringes for light reflected by the fluid surface. The Fizeau interferometry technique has been successfully used to measure the surface profiles of rotating He I and He II. Surface depressions like those predicted for a multiply quantized superfluid vortex were observed for the first time.

(8) Superfluid Helium Flow Through an Orifice Near Critical Velocity

Graduate Student: C. A. Waters

This experiment is designed to observe the small energy and momentum associated with the production of a single vortex ring in superfluid helium. To observe the momentum, a superconducting niobium cavity containing a pressure detecting diaphragm in one wall has been built. The motion of the diaphragm is detected as a change in the resonant frequency of the cavity. Vortex rings will be created by forcing liquid helium to flow through an orifice above the critical velocity.

(9) Properties of Superfluid Helium-3

Graduate Student: B. J. Neuhauser

Research Physicist: J. A. Lipa

The light isotope of helium, of atomic mass 3, has recently been shown to be a superfluid below a temperature of 2.5 millikelvins. Since the helium-3 atoms are Fermions, the understanding of the condensed state parallels the BCS treatment of superconductivity, but significant generalizations are required. Since the nuclei have a magnetic moment, the state displays interesting magnetic properties which can be probed using NMR techniques and SQUID magnetometry. In addition, the classical superfluid properties manifested in helium-4 are expected. We plan to measure some of these properties, in particular



NMR and second sound, in order to obtain a better understanding of the new state. In order to reach the ultra-low temperatures required, a first class helium-3/helium-4 dilution refrigerator is required, plus an extra stage of cooling using either adiabatic demagnetization of a paramagnetic salt, compressional cooling of helium-3 along its melting curve, or demagnetization of a nuclear spin system.

(10) Experiments in Very Low Magnetic Fields

Postdoctoral Fellow: B. Cabrera

We have obtained magnetic fields smaller than  $10^{-8}$  gauss in a cylindrical superconducting lead shield that is four inches in diameter and thirty inches long. This magnetic field level, an order of magnitude smaller than we had previously obtained, corresponds to at most a few flux quanta trapped in the superconducting shield. We are using a superconducting double point-contact magnetometer with a resolution of  $10^{-9}$  gauss to measure the very small magnetic fields. We have constructed an apparatus to measure the magnetic flux trapped in a superconducting cylinder 1/2 inch in diameter by 4 inches long. We have the sensitivity to see individual flux quanta penetrating the walls of this cylinder, and thus study the pinning of flux in superconductors. One of these shields has been used in conjunction with a detection coil coupled to a SQUID as a magnetic monopole detector. Our present sensitivity is 1/50 of a Dirac monopole. Our data to date is consistent with zero magnetic charge.

(11) Nuclear Polarization of  $\text{He}^3$

Graduate Student: M. A. Taber

We have used  $\text{He}^3$  optical pumping techniques to produce dilute polarized  $\text{He}^3$  and  $\text{He}^4$  gas mixtures. Such mixtures have been successfully condensed into a low magnetic field region and the precession of the  $\text{He}^3$  magnetization has been observed in an applied transverse field of  $10^{-4}$  gauss by use of a SQUID magnetometer. Initial magnetization has been greater than  $10^{-5}$  gauss with a signal to noise of 1000 to 1. We have completed a series of experiments to measure the spin-lattice

relaxation time ( $T_1$ ) of the liquid  $\text{He}^4$ -polarized  $\text{He}^3$  mixture under various conditions and as a function of applied field. The relaxation times vary from approximately 4 hours at 55  $\mu$  gauss to 35 hours at 1.8 mgauss for a bare Pyrex sample bulb. Using a solid  $\text{H}_2$  wall coating of ~40 molecular layers thick has yielded a relaxation time of 130 hours at 2.9 mgauss. At lower fields the relaxation times approached those of the bare bulb.

This field-dependent relaxation effect cannot be attributed to intrinsic relaxation in the liquid and experimental results have indicated that it is not due to magnetic field gradients or to the presence of electron paramagnetic impurities. The effect may be due to a previously undiscovered wall mechanism, but this possibility requires further study and experimental data.

These experiments are a continuation of an effort devoted to development of a  $\text{He}^3$  nuclear gyroscope.

(12) Magnetocardiology (Joint Project with Stanford Hospital)

Postdoctoral Fellow: J. P. Wikswo, Jr.

We are developing two new magnetic techniques for non-invasive clinical observation of human cardiac function. The first measures magnetic susceptibility changes associated with the motion of blood within the heart. The second technique involves the use of a superconducting gradient magnetometer to measure the magnetocardiogram, the magnetic field generated by the electrical activity of the heart. We have built a large magnetic shield and a computer signal-processing system. The clinical value of the magnetic field measurements will be determined by studying normal patients and patients with various cardiac diseases.

(13) Search for a Quark

Graduate Student: George LaRue

The purpose of this experiment is to search for fractionally charged particles (quarks) on superconducting niobium spheres supported by a magnetic field. The experiment measures the net electric charge on a niobium ball of mass approximately  $5 \times 10^{-5}$  gm. Fractionally

charged particles, if they are contained on a niobium ball, would be observable as a non-integral net charge on the ball. Measurements have been made on four niobium balls with a sensitivity of approximately  $\pm 0.02 e$ , where  $e$  is the electron charge. Forces simulating non-integral residual charges have been observed on these balls. The central issue in this experiment is to determine unambiguously whether or not these forces are due to fractional charges or are caused by spurious dipole sources. The apparatus has been rebuilt to increase the speed with which data can be assimilated and processed and to facilitate the identification of spurious dipole effects.

(14) Magnetic Field Penetration into Superconducting Thin Film Cylinders

Graduate Student: E. G. Wilson

A number of Sn cylinders, with wall thicknesses ranging from 5,000 Å to 10,000 Å, have been prepared by vacuum deposition onto quartz substrates. The interior penetration resulting from an axial external field is measured with a 30 MHz SQUID magnetometer as a function of temperature. (The external field is returned to zero before each change in temperature.) Three films have been produced which show nonlocal behavior, in that they are better fit by the nonlocal Pippard (or BCS) theory than by the London "local limit" theory. Other films fall into the local limit regime, due to the shortening of the mean free path produced by the film deposition process. The very small reversed interior magnetic field predicted by the theory for sufficiently non-local films (in an approximate temperature and film thickness regime) has not been seen. This is probably because (1) all of the films are more "local" than bulk Sn, and this reduces the predicted reversed field size to an even smaller value; and (2) pinholes, present to some extent in all of the films, produce a spurious positive signal.

(15) Microwave Josephson Effect Magnetometer

Graduate Student: D. E. Claridge

We have measured the 9 GHz small signal impedance of a dc biased superconducting niobium point contact. The impedance of the point,

measured as a function of the dc bias current shows qualitative agreement with the predictions of the resistively shunted junction model. The dependence of the impedance on the microwave signal level also follows the theory. The system has been improved and measurements are now in progress which should yield data suitable for quantitative comparison with theory. We will also attempt to measure the coefficient of the  $\cos \phi$  term in the quasiparticle conductance through its influence on the microwave impedance.

(16) Equivalence Principle Accelerometer

Postdoctoral Fellow: P. W. Worden, Jr.

Adjunct Professor: C. W. F. Everitt

The experiment is intended to test the application of cryogenic technology to a measurement of the uniqueness of free fall, particularly with regard to investigating the ultimate limitations to sensitivity and a possible earth-orbiting equivalence principle experiment. A pair of superconducting test masses of different materials are suspended in essentially frictionless linear magnetic bearings. The masses are cylindrical with dimensions optimized to minimize gravity gradient effects, and are free to move along the cylinder axis. An electronic control mechanism keeps each mass centered with respect to the casing by tilting the support plane provided by the magnetic bearing. The control efforts required to keep the masses centered are appropriately scaled and subtracted to one part in  $10^5$ , providing a signal proportional to any differential acceleration which may exist. The difference signal may then be recorded and Fourier analyzed to determine the relative amplitudes of the various frequency components.

The limiting sensitivity of the experiment on earth is set by seismic noise and the accuracy of the subtraction process. A difference of one part in  $10^{12}$  in the ratio of inertial to gravitational mass is estimated to be the limit of sensitivity on earth. In low earth orbit the sensitivity is limited by tidal sloshing of the liquid helium refrigerant and is probably one part in  $10^{17}$ .

(17) Relativity Gyroscope Experiment

Adjunct Professor: C. W. F. Everitt  
Research Physicists: J. T. Anderson  
J. A. Lipa  
Postdoctoral Fellow: B. Cabrera  
Visiting Postdoctoral Fellow: F. van Kann

In 1960 Professor Leonard Schiff of Stanford University suggested a new test of general relativity based on observing the precessions of very accurate gyroscopes in an earth-orbiting satellite. Since 1962, a group of physicists and engineers from the Hansen Laboratories and the Department of Aeronautics and Astronautics have been designing and developing the experiment using cryogenic techniques. A model of the flight gyroscope and liquid helium dewar has no been operating at Stanford for nearly three years. A low temperature run is in progress in Room 002 of the Physics basement.

(18) Superconducting Meson Channel

Professor: H. A. Schwettman  
Research Physicist: D. P. Boyd

A superconducting pion channel has been developed and is being constructed. It consists of two 10 ft. diameter torroidal superconducting magnets, each having 60 pancake forms. Cooling is achieved by conduction from liquid helium tubing placed on the edge of the coil forms. This novel application of large scale superconducting technology results in a large solid angle exceeding 1 steradian for the collection of pions. The purpose of the magnet is to collect and deliver pions for use in cancer therapy in a hospital facility.

(19) Time Variation of Fundamental Constants and Superconducting Cavity Stabilized Oscillator

Senior Research Associate: J. P. Turneure

The investigations involve the development of an X-band microwave oscillator (called the superconducting cavity stabilized oscillator or SCSO) with state of the art short term frequency stability and the application of this oscillator in an experiment to detect possible time variation of the fine structure constant.

The technique being pursued is to reference a commercial Gunn-effect oscillator (at 8.6 GHz) to a superconducting niobium cavity. Such a cavity is an excellent frequency reference because of the very narrow resonance line-width which can be obtained. For example, an X-band niobium cavity can be made with a resonance 100 times narrower than the atomic line width of the hydrogen maser. A discriminator of the intermediate frequency type has been developed to detect the cavity resonance frequency. The improvements which we have made in both the discriminator and the servo electronics cause the cavity itself to be the dominant source of frequency instability for the entire system.

The short term frequency fluctuations of the SCSO system have been extensively studied by mixing the outputs of two identical systems and performing spectrum analysis and period-time counting on the beat signal. It has been found that the rms fractional frequency fluctuations (referred to the operating frequency) are  $\sigma_y(\tau) = 6 \times 10^{-16}$  for a 100 sec averaging time. This is better than the performance of hydrogen and rubidium masers. The frequency drift of the SCSO system has also been measured via comparison with a cesium beam atomic clock for a period of about 2 weeks. The typical drift rate was  $1.5 \times 10^{-14}$  per day which is two decades lower than state of the art quartz crystal oscillators.

#### (20) Superconducting Microwave Cavities

Professor: H. A. Schwettman

Senior Research Associate: J. P. Turneaure

Research Associate: C. M. Lyneis

Several important problems have been encountered in the development of high Q, high field superconducting cavities which require a more complete understanding at a fundamental level. Investigations are in progress related to the surface resistance of superconductors, magnetic breakdown of the superconducting state, and electron loading phenomena in superconducting cavities. There are two questions related to the surface resistance of superconductors which are quite important and are currently being studied. These are the dependence of the surface resistance on material parameters such as the Landau-Ginzberg

parameter,  $\kappa$  (the ratio of the penetration depth,  $\lambda$ , and the coherence length,  $\xi$ ), and the electron free path,  $\ell$ ; and the possibility that fundamental loss mechanisms such as the generation of sound waves will set a limit on the smallest attainable surface resistance.

The maximum rf field level that can be attained in a superconducting cavity with high Q is often limited by a thermal-magnetic breakdown of the superconducting state. For high quality superconducting cavities such magnetic field limitations are characterized by an abrupt change in Q (by a factor of  $10^2$  and sometimes even  $10^5$ ) at a relatively well defined rf critical magnetic field,  $H_c^{rf}$ . To make progress in investigations of thermal-magnetic breakdown the superconducting surfaces must be better characterized. There are available to us a number of tools and methods to accomplish this including an Auger spectroscope, a scanning electron microscope, an electron microprobe, a transmission electron microscope, and other metallurgical equipment available at the Stanford Center for Materials Research. Also, we can utilize a number of physical measurements which help to characterize the surface including the dc resistance ratio, the normal state surface resistance, and temperature dependent surface reactance measurements.

Electron loading phenomena impose an important limitation on the field level that can be achieved in superconducting cavities at the frequencies of interest for an accelerator. At present in  $TM_{010}$  mode cavities at 1.3 GHz one is limited to electric field levels corresponding to an energy gradient of 2 MeV/ft by intense x-radiation that can exceed one R/hr measured at a distance one meter from the cavity. The observed x-radiation is thought to result from field emitted electrons, however, a detailed understanding of the phenomenon must include not only the field emission process, but also the electron dynamics in the cavity, and the secondary electron multiplication processes which follow electron impact with the cavity walls. Studies have shown that electron field emission in superconducting cavities is enhanced by geometric projections on the cavity surface and by resonant tunneling through surface states associated with adsorbed gases. Recent experiments have shown that electron dynamics and secondary processes can also have a profound

influence on the electron loading in superconducting cavities. For geometrically similar cavities resonant at different frequencies the electron dynamics are invariant (all trajectories, final energies, and final phases remain unchanged) if the electric field strength is scaled with frequency. Measurements on  $TM_{010}$  mode cavities at 1.3, 2.8 and 8.6 GHz indicate that electron loading at lower frequencies becomes an important problem at electric field values that are lower, strongly suggesting that the details of electron dynamics in the cavity must be considered.

Reference Publications:

1. L. Elias, W. M. Fairbank, J. M. Madey, H. A. Schwettman and T. Smith, "Observation of Stimulated Emission of Radiation by Relativistic Electrons in a Spatially Periodic Transverse Magnetic Field", Phys. Rev. Lett. 36, 717 (1976).



19. EXCITED STATE DYNAMICS AND ENERGY TRANSPORT IN MOLECULAR SOLIDS

M. D. Fayer, Assistant Professor, Chemistry

Graduate Students:

D. E. Cooper  
D. D. Dlott  
R. D. Wieting  
C. R. Gochanour

Undergraduate Students:

G. Eyring  
B. Whitcher

Agency Support

NSF/MRL through CMR  
ACS PRF 3074 G2  
Research Corporation  
Stanford Research Development Fund

Technical Objective:

To obtain an understanding of the nature of energy transport in solids: an area of great practical importance in addition to being one of the fundamental problems confronting both theoretical and experimental solid state physics. In particular, any time the collective interactions of a solid contribute to the propagation of a state or particle, both the coherent and incoherent mode of propagation must be considered in detail. This is true of singlet and triplet Frenkel excitons in molecular crystals which are under investigation here but identical considerations also apply to conduction electrons in metals and insulators, electrons and holes in semiconductors, lattice

or molecular vibrational energy transfer, the propagation of angular momentum in solids as spin waves or magnons and even in atomic diffusion, such as in the migration of  $^3\text{He}$  in solid  $^4\text{He}$ . At low temperatures ( $\sim 4^\circ\text{K}$ ) where phonon-exciton interactions are infrequent, propagation of coherent wave packets is expected to be the predominant energy transport mechanism. The velocity of propagation and therefore the distances over which energy can be rapidly transported is determined by the band dispersion and wave vector of the individual exciton states. Increased temperature results in a greater number of excitons with large group velocities able to travel long distances, but also results in increased phonon-exciton scattering which tends to reduce the wave packets coherence length. At high temperatures, ( $\sim 300^\circ\text{K}$ ) phonon-exciton scattering is expected to reduce the coherence length to less than one lattice site. Transport will take place by a random walk process, and therefore long range energy migration will be severely reduced. To date there is only very limited indirect experimental evidence that coherent migration occurs in triplet Frenkel excitons and these experiments are incapable of investigating the distances over which exciton migration occurs. Singlet Frenkel excitons which should exhibit rapid coherent migration due to their large exciton band dispersions are of particular interest because they will be able to transport energy over long distances between phonon-exciton scattering events.

### Approach:

By combining picosecond experiments and slower optical excitation techniques with steady state optical experiments a variety of phenomena related to energy transport in molecular crystals are being investigated. These phenomena include the strength of intermolecular interactions responsible for exciton transport, the rate and temperature dependence of exciton-phonon scattering, the mode of exciton transport and the directional nature of the transport. In addition the actual velocity of exciton propagation is being examined on a picosecond time scale.

The steady state experiments involve the observation of the temperature dependence of the intensity of phosphorescent emission from low concentration shallow "traps." As the temperature is increased from 1.3°K to 4.2°K the intensity of trap emission is reduced due to an increased rate of phonon assisted promotion of the trapped excitation to the exciton band. For the correct set of physical conditions the exciton band states and the trap states are in thermal equilibrium, and therefore the trap emission intensity which is proportional to the trap population is determined by the systems partition function. The intermolecular interaction matrix element and the exciton density of states have been obtained by fitting the observed trap intensity temperature dependence to the partition function. Thus the important static band parameters are determined. Using these in conjunction with literature reported triplet exciton E.S.R. spectra for the crystal, the mean exciton coherence length for the one-dimensional solid 1,2,4,5-tetrachlorobenzene has been determined. A coherence length of 240,000 Å was

measured at 3.2°K. This is the first reliable determination of a macroscopic exciton coherence length in a molecular solid. In another set of experiments performed on triplet exciton states, time dependent observation of phosphorescent emission decay and of delayed fluorescence produced by triplet-triplet annihilation of mobile excitons permitted the symmetry of the exciton state to be determined and the ratios of triplet exciton spin sublevels radiative rate constants and intersystem crossing rates to be measured.

The dynamics of exciton transport in the low temperature coherent region, the high temperature random walk region and the intermediate region, are capable of being directly investigated utilizing the picosecond transient-grating technique recently developed by A. E. Siegman. In this technique, two ultra-short light pulses generated with a mode-locked laser are propagated along different paths and overlapped in the sample, i.e. a molecular crystal with a singlet absorption at the laser wavelength. The interference of the two beams produces a sinusoidally spatially varying intensity distribution in the crystal which results in the production of singlet excitons in the regions where the intensity is large. A third pulse of light from the laser (with a different wavelength) is directed into the sample at a desired time interval after the initial excitation. This probe pulse is diffracted off the "grating" established by the first two pulses at a unique angle, and the intensity of the diffracted beam is measured. As exciton migration proceeds, the "valleys" between the regions of high exciton concentration are filled in and the amplitude of the diffracted probe pulse is reduced. Since

the spatial distribution of the initial intensity is known and the time of the probe pulse is known, the rate of exciton migration can be directly measured. Detailed preliminary computer calculations indicate that the time scale of this technique is appropriate to the measurement.

Application of the transient grating technique to the exciton migration problem provides a unique tool for the study of a wide range of effects. By varying the sample temperature, the exciton and phonon population distributions are both altered. Temperature dependent velocities, coherence lengths, and phonon-exciton scattering are therefore opened to direct study. In addition, by varying the alignment of the transient grating relative to the sample crystallographic axes, the anisotropy in the directional rate of energy transport may be mapped out. This is particularly interesting in application to "one-dimensional" solids. Further, introduction of low energy impurities into the sample will localize the exciton on a particular lattice site for a period of time and therefore hinder the migration. Temperature dependent phonon interactions with these localized states will promote an excitation back into the exciton band where it will again be mobile. The concentration, temperature, and trap depth dependence of the exciton localization are also opened for study.

In addition to the transient-grating experiments, other picosecond techniques are being employed to investigate the individual processes of localization of an exciton wave packet by an impurity, promotion of a localized state to a delocalized band state, exciton-phonon scattering, the effect of high energy potential barriers on exciton

migration and the transfer of excitation between unlike chromophores. The picosecond work employs a tunable mode-locked flash lamp pumped dye laser. A five picosecond pulse of visible light is selected from the mode-locked pulse train and is doubled into the UV. The UV pulse is then used to both excite and probe the dynamics of the above processes. The phenomena are investigated in the temperature range 1.5°K to 300°K using a variable temperature liquid helium dewar system.

#### Reference Publications:

1. M. D. Fayer and C. B. Harris, "Coherent Energy Migration in Solids. I. Band-Trap Equilibrium at Boltzmann and non-Boltzmann Temperatures," Physical Review B 9, 748 (1974).
2. M. D. Fayer and C. B. Harris, "The Decay and Localized States into Delocalized Band States. Theory and Preliminary Experimental Investigations Using Optically Detected Electron Spin Coherence," Chemical Physics Letters, 25, 149 (1974).
3. C. B. Harris and M. D. Fayer, "Coherent Energy Migration in Solids. II. Spin-resonance Absorption in Coherent-Wave-Packet States and the Effects of Phonon-Exciton Scattering," Physical Review B 10, 1784 (1974).

## 20. CRYSTAL GROWTH RESEARCH

R. S. Feigelson, Senior Research Associate, CMR

### Professional Associates:

R. C. DeMattei  
R. A. Huggins  
R. K. Route  
I. V. Zubeck

### Agency Support:

NSF/MRL through CMR  
ERDA through CMR  
ARPA through CMR

### Technical Objective:

To develop sufficient understanding of crystal growth processes to enable the preparation of a wide variety of materials with closely controlled properties.

### Approach:

Through careful evaluation of thermodynamic and kinetic factors compiled with detailed analysis of experimental parameters, optimized growth conditions can be achieved for most materials. Studies of phase equilibria, nucleation, growth anisotropy, interface morphology and thermal and mechanical stresses are particularly important parameters in crystal growth.

### Research Report:

#### (1) Growth of Large [013] $\text{LiNbO}_3$ Crystals with Low OH Absorption

Technical Associate: W. L. Kway

$\text{LiNbO}_3$  has unique electro-optic properties which make it useful in a number of important optical applications including phase matched second harmonic generation and parametric generation. Recently an

application for a high energy  $1.06\text{ }\mu\text{m}$  pumped  $\text{LiNbO}_3$  parametric oscillator required crystals up to 59 cm in length at a propagation angle  $45^\circ$  to the optic axis in the negative yz gradient. The quality of standard [00.1] oriented boules was not sufficient to yield useful material nor was standard high optical quality [01.0] boules suitable because they could not be grown large enough to yield the required crystal size. A program was therefore initiated to grow crystals along an axis more closely aligned with the propagation direction. Techniques were subsequently developed for growing along the [01.4] ( $38^\circ$  from the [00.1]) and the [01.3] ( $47^\circ$  from the [00.1]). The optical quality of these crystals was comparable to the highest quality material produced previously. Excellent optical parameter oscillators have been fabricated from the material with very little loss of material in cutting.

Typically,  $\text{LiNbO}_3$  cannot be effectively tuned throughout the near infrared region due to an optical absorption band near  $2.7\text{ }\mu\text{m}$  due to OH impurities in the crystals. A special technique has been developed to reduce the OH adsorption by an order of magnitude, which now allows tunable oscillators to operate throughout this region.

(2) The Influence of Interface Shape on the Crystal Quality of Bridgman Grown  $\text{CdGeAs}_2$

Professional Associate: R. K. Route  
Technical Associate: H. W. Swarts

$\text{CdGeAs}_2$  is currently the most promising material for use as a mixing crystal or OPO crystal in a tunable IR laser system. It is continuously phase matchable from 2 to  $18\text{ }\mu\text{m}$  and possesses a higher burn density than other potentially usable materials such as  $\text{AgGaSe}_2$  and  $\text{Ag}_3\text{AsS}_3$ . However, techniques have not yet been developed to grow large, high optical quality crystals on a reproducible basis. Cracking associated with polycrystallinity and anisotropic thermal expansion, and poor optical quality are currently the two major problems.

Control over the occurrence of polycrystallinity has recently been achieved through a detailed study of interface shape and the



factors which influence it. In decanting experiments carried out in typical Bridgman melt growth systems, unfavorable concave interface shapes were consistently found. This type of interface shape is known to have an adverse effect on grain selection, and is thought to be responsible for the high occurrence of polycrystallinity in typical Bridgman systems.

An analysis of heat flow in a Bridgman system was carried out to determine which factors influence interface shape. The results indicated that the thermal conductivity of solid  $\text{CdGeAs}_2$  must be much smaller than that of the melt in order to account for the results observed, and that a discontinuous temperature gradient would be required to produce a more suitable interface shape. In an appropriately designed two zone furnace, planar and, in some cases, slightly convex interface shapes were achieved. Crystals grown under these conditions were found to be essentially free of polycrystallinity. Consequently, the extensive cracking associated with grain boundaries in polycrystalline boules has been eliminated.

#### Reference Publications:

1. R. S. Feigelson and R. K. Route, "Improved Techniques for the Growth of the Chalcopyrite Compounds  $\text{AgGaSe}_2$  and  $\text{CdGeAs}_2$ ", Conference on Lasers for Isotope Separation, ERDA/LASL, Albuquerque, New Mexico, April 1976.
2. R. S. Feigelson, R. K. Route and H. W. Swarts, "The Influence of Interface Shape on the Crystal Quality of Bridgman Grown  $\text{CdGeAs}_2$ ", American Association for Crystal Growth/West Conference, Los Angeles, California, June 1976.
3. R. S. Feigelson, "The Growth of Ternary Semiconductor Crystals Suitable for Device Applications", J. Physique Colloq. 36, C3 (1975).

#### (3) Elimination of Optical Scattering Defects in $\text{AgGaS}_2$ and $\text{AgGaSe}_2$

Professional Associate: R. K. Route

Technical Associate: R. J. Raymakers

Silver gallium disulfide ( $\text{AgGaS}_2$ ) and silver gallium diselenide ( $\text{AgGaSe}_2$ ) are potentially useful materials for non-linear optical

applications. They have high non-linear coefficients and are phase matchable over a broad portion of the IR spectrum.  $\text{AgGaS}_2$  is transparent from 0.6 to 13  $\mu\text{m}$ , and  $\text{AgGaSe}_2$  from 0.7 to 17  $\mu\text{m}$ . Poor crystal quality and variable optical transparency, however, made early crystals unsuitable for device application.

Phase equilibrium studies combined with detailed optical transmission measurements have been utilized to totally eliminate the problem of variable optical transparency in these materials. In the as-grown state, microscopic scattering centers (precipitates rich in Ga and S or Se) cause a "milky" appearance and strongly anisotropic scattering around 1.0  $\mu\text{m}$ . Effective optical absorption due to scattering phase impurity absorption can vary in both from 0.1  $\text{cm}^{-1}$  to greater than 5  $\text{cm}^{-1}$ .

Post-growth heat treatments have been developed which totally eliminate the scattering centers in both  $\text{AgGaS}_2$  and  $\text{AgGaSe}_2$ . In one technique, crystals are rapidly quenched from single phase regions which exist in a temperature range just below their respective melting points. In the other, crystals are annealed at elevated temperatures in the presence of excess  $\text{Ag}_2\text{S}$  or  $\text{Ag}_2\text{Se}$  in order to compensate for the excess Ga and S or Se. Both techniques are completely effective in eliminating the microscopic scattering centers which are the principal cause of short wavelength optical absorption in these materials.

#### Reference Publications:

1. R. K. Route, R. S. Feigelson, R. J. Raymakers and M. M. Choy, "Elimination of Optical Scattering Centers in  $\text{AgGaS}_2$  and  $\text{AgGaSe}_2$ ", J. Crystal Growth 33, 239 (1976).
2. R. S. Feigelson and R. K. Route, "Improved Techniques for the Growth of the Chalcopyrite Compounds  $\text{AgGaSe}_2$  and  $\text{CdGeAs}_2$ ", Conference on Lasers for Isotope Separation, ERDA/LASL, Albuquerque, New Mexico, April 1976.
3. R. S. Feigelson, R. K. Route and H. W. Swarts, "The Influence of Interface Shape on the Crystal Quality of Bridgman Grown  $\text{CdGeAs}_2$ ", American Association for Crystal Growth/West Conference, Los Angeles, California, June 1976.

4. R. S. Feigelson, "The Growth of Ternary Semiconductor Crystals Suitable for Device Applications", J. Physique Colloq. 36, C3 (1975).

#### (4) Growth of Gallium and Indium Phosphide

Professional Associate: I. V. Zubeck

Gallium phosphide (GaP) and indium phosphide (InP) are two semiconductor compounds in which there is a great deal of current interest. Electrochemical crystallization offers another potential technique for the synthesis of device quality material of these compounds. While the electrochemical synthesis of both GaP and InP has been reported, the systems have not been well characterized and no major effort has gone into the production of device grade material. A further study of these materials has begun.

Indium phosphide has been deposited on silicon at 800°C from a sodium metaphosphate ( $\text{NaPO}_3$ ) based melt containing indium oxide ( $\text{In}_2\text{O}_3$ ) and sodium fluoride (NaF). Electrodeposition of this material has the advantage of operating at temperatures well below the melting point of InP where a phosphorus pressure of 27 atmospheres is needed to stabilize the compound. Substitution of gallium oxide ( $\text{Ga}_2\text{O}_3$ ) for  $\text{In}_2\text{O}_3$  results in the deposition of GaP. Gallium phosphide can also be deposited from a lower melting (650°C) melt based on a lithium chloride (LiCl)-potassium chloride (KCl) eutectic containing  $\text{NaPO}_2$  and  $\text{Ga}_2\text{O}_3$ . This latter melt has been used to deposit 1 mm layers of GaP on silicon.

Study study has also demonstrated that melts can be purified electrochemically. Iron was removed from the GaP melt by a pre-electrolysis at a potential slightly below that required to deposit GaP. After a period of 48 hours virtually all of the iron impurity was eliminated.

#### Reference Publications

1. J. J. Cuomo and R. J. Gambino, J. Electrochem. Soc. 115, 755 (1968).

2. I. V. Zubeck and R. S. Feigelson, "Electrocrystallization of GaP", presented to American Association of Crystal Growth/ West 1976, June 4, 1976.

(5) Growth of Single Crystal Lanthanum Hexaboride ( $\text{LaB}_6$ )

Professional Associates: R. A. Huggins, I. V. Zubeck  
Technical Associate: P. Pettit

Lanthanum hexaboride is a hard, refractory material. It is difficult to produce in single crystal from by conventional techniques due to the elevated temperatures necessary for its growth. It has, however, been synthesized electrochemically, at  $800^\circ\text{C}$  from a boron oxide ( $\text{B}_2\text{O}_3$ ) based melt containing lanthanum oxide ( $\text{La}_2\text{O}_3$ ) and lithium fluoride ( $\text{LiF}$ ). The current effort has been directed to developing an understanding of the parameters necessary to grow reproducible polycrystalline clusters and ultimately to grow large seeded single crystals by molten salt electrochemical techniques.

Initial nucleation and growth experiments were performed using a gold wire cathode (crystals grow at the cathode). Under these conditions there was always multinucleation. At low current densities (below  $30 \text{ ma/cm}^2$ ), these nuclei grew by the propagation of pyramidal features which always appear in the  $\{100\}$  faces. At somewhat higher current densities ( $\sim 50 \text{ ma/cm}^2$ ), the crystals exhibit "hopper" growth; and ultimately, at very high current densities ( $> 100 \text{ ma/cm}^2$ ) dendrites form along the  $[111]^{(2,3)}$ . By careful control of the nucleation and growth conditions clusters of crystallites containing individual crystallites of 4 mm on a side could be grown.

Based on these results, the seeded growth of large single crystals of  $\text{LaB}_6$  was undertaken. The seed material (2 mm x 3 mm) was obtained from large grain, zone melted material. Growth at  $18 \text{ ma/cm}^2$  for 200 hours produced a single crystal 5 mm x 5 mm x 6 mm. This is the first report of the growth of a single crystal of  $\text{LaB}_6$  of this size by any technique.

The study of  $\text{LaB}_6$  also contributed to the understanding of the rate controlling process during electrochemical crystallization.

#### Reference Publications:

1. L. Andrieux, Ann. Chim. 12, 424 (1929).
2. D. Elwell, I. V. Zubeck, R. S. Feigelson and R. A. Huggins, J. Crystal Growth 29, 65 (1975).
3. I. V. Zubeck, R. S. Feigelson and R. A. Huggins, "The Growth of Lanthanum Hexaboride Crystals by Electrolysis of Molten Salts", presented to the Third American Conference on Crystal Growth (ACCG III), July 13-17, 1975.
4. I. V. Zubeck, R. S. Feigelson, R. A. Huggins and P. A. Pettit, "The Growth of Lanthanum Hexaboride Single Crystals by Molten Salt Electrolysis", J. Crystal Growth (to be published).
5. D. Elwell, R. C. DeMattei, I. V. Zubeck, R. S. Feigelson and R. A. Huggins, J. Crystal Growth 33, 232 (1976).

#### (6) The Electrochemical Czochralski Technique (ECT)

Professional Associates: R. C. DeMattei, R. A. Huggins

A technique combining molten salt electrocrystallization and the Czochralski method of crystal growth has been developed. In this Electrochemical Czochralski Technique (ECT) thermal driving forces are replaced by the potential difference maintained between the crystal (cathode) and an anode inserted in the melt. This relatively low temperature technique is particularly useful for producing boules of electrically conducting material which can not be grown by the conventional technique due to problems associated with thermal decomposition or with non-congruent melting systems. Due to the isothermal nature of ECT, control of the diameter of the growing material is achieved by balancing the pull rate and the total current.

Using the cubic phase of sodium tungsten bronze ( $\text{Na}_x\text{WO}_3$ ,  $0.38 < x < 0.9$ ) as a model system, crystals were grown on  $\langle 111 \rangle$  oriented seeds under an inert atmosphere at  $750^\circ\text{C}$ . These crystals exhibited triangular cross sections and, unlike crystals grown by the normal Czochralski technique, has faceted interfaces.

Due to the faradaic nature of the growth process, the weight of material deposited (Wt) is given by

$$\text{Wt} = \frac{\text{Mw} \epsilon Q}{x F}$$

where  $M_w$  is the molecular weight of the compound,  $\epsilon$  is the deposition efficiency (0.92 for  $Na_xWO_3$ ),  $Q$  is the charge passed in coulombs,  $x$  is the stoichiometry coefficient in  $Na_xWO_3$  and  $F$  is Faraday's constant. For crystals growing in the [111], this expression can be modified to give the distance ( $d$ ) across one of the sides of the triangular cross section in terms of current ( $I$ ) and pull rate ( $dy/dt$ )

$$d = \left[ \frac{M_w \epsilon I}{0.75x f \rho \frac{dy}{dt}} \right]^{1/2}$$

where  $\rho$  is the density of the material. This equation has been used to predict the cross section of  $Na_xWO_3$  crystals over a wide range of currents, pull rates and compositions with a  $\pm 10\%$  uncertainty.

The influence of seed rotation rate  $W$  on pull rate was also studied. Up to 32 rpm, the pull rate increased with increasing rotation rate

$$dy/dt = 2.25 + K W^{1.17}$$

Above 48 rpm, a flow separation occurs at the interface and the crystal morphology deteriorated.

#### Reference Publications:

1. R. C. DeMattei, R. A. Huggins and R. S. Feigelson, "Crystal Growth by the Electrochemical Czochralski Technique", presented at Third American Conference on Crystal Growth (ACCG III), July 13-17, 1975.
2. R. C. DeMattei, R. A. Huggins and R. S. Feigelson, "Crystal Growth by the Electrochemical Czochralski Technique", J. Crystal Growth (to be published).

## 21. MACROMOLECULAR RESEARCH

P. J. Flory, J. G. Jackson-C. J. Wood Emeritus Professor  
of Chemistry

### Professional Associates:

†A. Abe  
J. Mark  
†M. Mutter  
D. Napper  
H. Neidlinger  
E. Saiz  
†U. W. Suter

### Graduate Students:

W. A. Boettner	†Left during report period
*C. W. Carlson	*Received Ph.D. during report
†L. C. DeBolt	period.

### Agency Support:

AFOSR 73-2441-A,B,C  
NSF DMR-73-07655 A02, A02

### Technical Objective:

To develop a better basis for understanding macromolecules and for interpreting their behavior.

### Approach:

Currently, investigations are under way in the following areas:

1. Rubber elasticity and the effect of dilation on the stored elastic free energy. Theory of rubber elasticity.
2. Statistical mechanics of stiff chains.

3. The configuration and elastic properties of elastin.
4. Investigations on the optical anisotropies of polystyrene and its oligomers, on the calculation of proton NMR chemical shifts in polystyrene and in poly(methyl methacrylate), and on the optical anisotropies of chlorinated alkanes related to poly(vinyl chloride).
5. Electric birefringence of oligomers and polymers.
6. Theory of cyclization of chain molecules.
7. X-ray and neutron scattering by polymers.
8. Configurational statistics of polymer chains.

#### Reference Publications:

1. P. J. Flory and D. Y. Yoon, "Moments and distribution functions for polymer chains of finite length. I. Theory," J. Chem. Phys., 61, 5358-5365 (1974)
2. D. Y. Yoon and P. J. Flory, "Moments and distribution functions for polymer chains of finite length. II. Polymethylene," J. Chem. Phys., 61, 5366-5380 (1974).
3. Paul J. Flory and Yoh-Ichi Tatara, "The Elastic Free Energy and the Elastic Equation of State: Elongation and Swelling of Polydimethylsiloxane Networks," J. Polymer Sci.: Polymer Phys. Ed., 13, 683-702 (1975).
4. Paul J. Flory, "Spatial Configuration of Macromolecular Chains," Science, 188, 1268-1276 (1975).
5. D. Y. Yoon and P. J. Flory, "Small angle neutron and X-ray scattering by poly(methyl methacrylate) chains," Polymer, 16, 645-648 (1975).



6. U. W. Suter and P. J. Flory, "Conformational Energy and Configurational Statistics of Polypropylene," *Macromolecules*, 8, 765-775 (1975).
7. D. Y. Yoon, P. R. Sundararajan, and P. J. Flory, "Conformational Characteristics of Polystyrene," *Macromolecules*, 8, 776-783 (1975).
8. D. Y. Yoon, U. W. Suter, P. R. Sundararajan, and P. J. Flory, "Conformational Characteristics of Poly(methyl acrylate)," *Macromolecules*, 8, 784-789 (1975).
9. Paul J. Flory and Vincent W. C. Chang, "Moments and Distribution Functions for Poly(dimethylsiloxane) Chains of Finite length," *Macromolecules*, 9, 33-40 (1976).
10. Joan C. Conrad and Paul J. Flory, "Moments and Distribution Functions for Polypeptide Chains. Poly-L-alanine," *Macromolecules*, 9, 41-47 (1976).
11. Paul J. Flory, "Statistical Thermodynamics of Random Networks," *Proc. Roy. Soc.*, in press.
12. P. J. Flory, U. W. Suter and M. Mutter, "Macrocyclization Equilibria. I. Theory," *J. Amer. Chem. Soc.*, in press.
13. P. J. Flory, U. W. Suter and M. Mutter, "Macrocyclization Equilibria. II. Poly(dimethylsiloxane)," *J. Amer. Chem. Soc.*, in press.
14. M. Mutter, U. W. Suter and P. J. Flory, "Macrocyclization Equilibria. III. Poly(6-aminocaproamide)," *J. Amer. Chem. Soc.*, in press.
15. Akihiro Abe, J. W. Kennedy, and P. J. Flory, "Persistence Vectors and Higher Moment Tensors of Polyoxyalkanes," *J. Polym. Sci., Polym. Phys. Ed.*, in press.

16. D. Y. Yoon and P. J. Flory, "Persistence Vectors for Polypropylene, Polystyrene and Poly(methyl methacrylate) Chains," J. Polym. Sci., Polym. Phys. Ed., in press.
17. Akihiro Abe and James E. Mark, "Conformational Energies, and the Random-Coil Dimensions and Dipole Moments of the Polyoxides  $\text{CH}_3\text{O}[(\text{CH}_2)_y\text{O}]_x\text{CH}_3$ ," J. Amer. Chem. Soc., in press.
18. Akihiro Abe, "Dipole Moments of Vinyl Polymers with Flexible Side Chains," J. Polym. Sci., in press.
19. Akihiro Abe, "Conformational Analysis of 2-Methoxytetrahydropyran in Relation to the Anomeric Effect," J. Amer. Chem. Soc., in press.

## 22. METAL FATIGUE

Henry O. Fuchs, Professor Emeritus, Mechanical Engineering

### Graduate Students:

Varouj Baghdasarians  
Frank Tanner  
Alonso Velez

### Support:

Deere & Company (Materials Engineering Department)  
Metal Improvement Company

### Technical Objectives:

Our main objective deals with the effects of complex variations of states of stress (or strain) on metal structures. This includes for instance shifting principal axes or out-of-phase variations of principal stresses. Rotating shafts transmitting power through gears are examples of structures subject to such stress variations. We want to gain understanding of the effects and, if possible, devise criteria useful in design.

Secondary objectives are refinements of the cumulative damage work completed last year and measurement of the effects of shotpeening.

### Approach:

Conceptually we approach the problem of complex stress variations by considering changes in direction and magnitude of the stress or strain deviator, and by considering changes in direction and magnitude of the adjusted maximum resolved shear stress.

Experimentally we will use specimens so designed that the locations of failures indicate the relative importance of different plausible criteria.

### Research Report

1. Specimens, fixtures, and test machines are being designed for exploratory tests on fatigue under complex stress variations. The tests are intended to demonstrate that our approach is feasible and far more economical than classic methods. If we can show this we hope to obtain

the substantial support required to develop criteria applicable in design.

2. We are also doing research on the measurement of the effects of self-stresses produced by shotpeening.

Publications:

Papers resulting from our older work on cumulative damage in fatigue have been accepted for publication in

ASTM Special Publication on Crack Propagation

SESA Experimental Mechanics

SAE Transactions

but have not yet appeared in print.

23. SUPERCONDUCTING POWER TRANSMISSION LINE MATERIALS RESEARCH

T. H. Geballe, Professor, Applied Physics and Materials Science and Engineering

M. R. Beasley, Associate Professor, Applied Physics and Electrical Engineering

Professional Associates:

T. W. Barbee, Jr.

R. H. Hammond

C. N. King

R. B. Zubeck

R. E. Howard

Graduate Students:

S. Kim

D. F. Moore

R. H. Norton

J. R. Salem

R. A. Thomas

Agency Support:

NSF-RANN AER72-03572

EPRI/ERDA E(49-18)-1569

ERDA E(04-3)-326-DA

Technical Objectives:

To produce prototype conductors for potential use in superconducting power transmission lines which demonstrate the technical and economic feasibility of using superconductors in underground power transmission.

Approach:

Emphasizes research for new superconducting materials and new methods of incorporating superconductors into practical cables with all the desired electrical properties. Focus is presently on multilayered composites of  $Nb_3Sn$  and normal metal (pinning) barriers. The physics of well-defined structures are studied at a fundamental level in order to gain an understanding of the important parameters governing critical current, ac losses and stability.

Research Reports:

### (1) Conductor Fabrication

The materials science of these conductors is being systematically studied using the considerable control over the composition and deposition conditions possible with our dual electron beam coevaporation system. Most importantly it has been found that the good surfaces and growth morphologies which are obtained under optimal deposition conditions in thin single layers can be maintained in the much thicker multi-layer composites desired for superconducting power transmission line application. The observed behavior under the different deposition conditions can be largely understood on the basis of recent fundamental work on the surface and growth morphologies of vacuum deposited thin films. As a result, our efforts now have a firmer scientific base and need not be so empirical.

#### Reference Publication:

R. B. Zubeck, C. N. King, D. F. Moore, T. W. Barbee, Jr., A. B. Hallak, J. Salem and R. H. Hammond, "Growth Morphologies of Thick Films of  $\text{Nb}_3\text{Sn}$  Formed by Electron Beam Evaporation," Presented at the Int. Conf. on Metallurgical Coatings, April 5-9, 1976 San Francisco

### (2) Critical Currents and AC Losses

The critical currents and ac losses of a series of layered composites have now been measured. The finely layered composites are found to have critical currents that increase linearly from some base value as the density of pinning layers increases. Critical current densities as large as  $\sim 9 \times 10^6 \text{ A/cm}^2$  have been obtained in this manner. In addition total current capacity (current per unit width of conductor) as high as  $5000 \text{ A/cm}$ , which is in the fault level regime expected in real transmission lines, has been achieved. Unfortunately ac instabilities are present, but since no attempt has yet been made to stabilize these conductors, improvement is expected. The observed ac losses are acceptable for power line application.

#### Reference Publications:

- (1) R. E. Howard, C. N. King, R. H. Norton, R. B. Zubeck, T. W. Barbee, and R. H. Hammond, "Critical Current and AC Loss of Coevaporated  $\text{Nb}_3\text{Sn}$  Superconductors," to appear in Adv. Cryo. Eng.

- (2) R. H. Norton, R. E. Howard, and R. E. Schwall, "A Technique for Measuring AC Losses in Thin Film Superconductors," to appear in Adv. Cryo. Eng.

## 24. LOW TEMPERATURE PROPERTIES OF MATERIALS

T. H. Geballe, Professor, Applied Physics and Materials Science and Engineering

### Professional Associates:

T. W. Barbee, Jr.  
R. H. Hammond  
R. E. Howard  
C. N. King  
R. B. Zubeck

### Graduate Students:

S. R. Early	R. H. Norton
A. B. Hallak*	M. C. O'Connor
J.M.E. Harper*	B. Robinson
G. R. Ierley	J. R. Salem
T. J. Jach*	G. R. Stewart*
S. Kim	R. A. Thomas
D. B. Kimhi	R. G. Young**

\* Received Ph.D. during report period

\*\* Received M.S. during report period

### Agency Support:

AFOSR 73-2435B  
NSF DMR74-21982  
NSF/MRL through CMR

### Technical Objective:

To prepare new and unusual superconducting and magnetic compounds and composite structures and to study the mechanisms and interactions responsible for their behavior.

### Approach:

Techniques such as electron-beam evaporation, arc melting, and vapor transport are used to prepare crystals, compounds or materials of interest. Their electronic properties are then correlated with their structural properties by investigating superconducting transitions, heat capacities, optical and transport properties including tunneling.

### Research Reports:

- (1) Electronic, Lattice, and Magnetic Properties of Solids at Low Temperatures



Graduate Students: S. R. Early  
J.M.E. Harper  
G. R. Ierley  
T. J. Jach  
B. Robinson  
G. R. Stewart  
R. A. Thomas

Small sample (1-100 milligram) calorimetry techniques developed by our group are being used to study a wide variety of low temperature energy spectra in solids. A search for size quantization of the electronic energy levels in small particles,  $\sim 15\text{\AA}$ , of Pt found strong indications for the existence of this phenomenon. The onset of charge density waves in  $2\text{H-NbSe}_2$  was found to give rise to a small second order phase transition in the specific heat lending support to the suggestion of there being only a small part of the Fermi-surface involved. The lattice contribution to the low temperature heat capacity has been studied in systems that show significant departures from Debye theory at relatively low temperatures. In the case of layered compounds such as  $2\text{H-TaSe}_2$  this is due to very anisotropic bonding forces in the solid. More detailed information on the phonon spectrum is being obtained for superconducting materials through the use of tunneling techniques. By using ultra high vacuum techniques, the first successful application of the tunneling technique to obtain the phonon spectrum in both the amorphous and crystalline states of N has been accomplished.

Reference Publications:

- (1) T. Jach, "Detection of Nuclear Quadrupole Resonances via Induced Longitudinal Magnetization," Appl. Phys. Lett. (Sept. 1975).
- (2) G. R. Stewart, "Size Effects in the Heat Capacity of Small Platinum Particles Imbedded in Silica," submitted to Phys. Rev.
- (3) T. Chen, J. W. Allen, and G. R. Stewart, "Magnetic and Electric Properties of MnSb," presented at 21st Annual Conference on Magnetism and Magnetic Materials, Philadelphia, December 1975.
- (4) M. Barmatz, L. R. Testardi, F. J. Di Salvo, and J.M.E. Harper, "The Elastic Behavior of  $2\text{H-TaSe}_2$ ," to be published in Phys. Rev.
- (5) C. W. Chu, T. H. Geballe, S. Early, R. E. Schwall, and A. Rusakov, "High Pressure Metallic Phase in Cuprous Chloride Single Crystals," J. Phys. C 8 1241 (1975).

- (6) J.M.E. Harper, T. H. Geballe, and F. J. Di Salvo, "Heat Capacity of  $2H-NbSe_2$  at the Charge Density Wave Transition," Phys. Letters 54A 27 (1975).
  - (7) R. E. Schwall, G. R. Stewart, and T. H. Geballe, "Low Temperature Specific Heat of Layered Compounds," J. Low Temp. Phys. 22, 557 (1976).
  - (8) N. Bilir, W. A. Phillips, and T. H. Geballe, "Thermal Properties of Boron Phases," in Proceedings of 14th International Conference on Low Temperature Physics, LT-14, Helsinki, August 1975.
  - (9) A. R. Sweedler, C. L. Snead, L. Newkirk, F. Valencia, T. H. Geballe, R. E. Schwall, B. T. Matthias, and E. Corenswit, to be published in Proceedings of International Conference on Radiation Effects for Fusion Reactors, Gatlinberg, 1975.
  - (10) B. Robinson, T. H. Geballe, and J. M. Rowell, "Tunneling Study of Quench Condensed Superconducting Transition Metals," Bull. Am. Phys. Soc. 21, 402 (1976).
- (2) A15 Synthesis and Properties
- Graduate Students: A. B. Hallak  
J.M.E. Harper  
M. C. O'Connor
- Professional Associates:  
R. H. Hammond  
R. B. Zubeck

This family comprises all the known high temperature superconductors. The synthesis of various members by means of independently controllable electron beams has been shown to be highly controllable insofar as stoichiometry and texture are concerned. The phase diagram of  $Nb_3Ge$  has been explored at temperatures below  $1000^{\circ}K$ . The presence of oxygen in the vacuum chamber has a surprisingly large effect upon the crystal perfection and superconducting temperature. A small concentration is essential to obtain optimum properties. Heat capacity measurements on films of  $Nb_3Ge$  prepared by L. Newkirk at Los Alamos which have superconducting transition onsets of  $>21^{\circ}K$  have a much lower density of states than  $Nb_3Sn$ . No evidence for the very sharp structure in the density of states in  $Nb_3Sn$ , which is postulated by all the models in order to explain the temperature dependent spin paramagnetism and related effects, has been found by the technique of optical absorption.

Reference Publications:

- (1) J.M.E. Harper, T. H. Geballe, L. R. Newkirk, and F. A. Valencia, "Low Temperature Thermal and Electrical Properties of Chemical-Vapor-Deposited  $\text{Nb}_3\text{Ge}$ ," J. Less-Common Metals 43, 5 (1975).
- (2) A. Hallak, R. H. Hammond, R. B. Zubeck, and T. H. Geballe, "Superconductivity and Range of Existence of the  $\text{A15}$  Phase in the  $\text{Nb-Ge}$  System," Bull. Am. Phys. Soc. 21, 340 (1976).

## 25. ION IMPLANTATION IN SEMICONDUCTORS AND PROTON-ENHANCED DIFFUSION

J. F. Gibbons, Professor, Electrical Engineering

### Graduate Students:

E. Ammar  
J. R. Anderson\*  
J. C. Bean\*  
A. Chu  
A. Gat  
T. Herman  
A. Lidow  
S. W. Mylroie\*  
H. D. Rodeen  
D. Smith  
R. E. Tremain\*  
F. C. Wu

\*Received Ph.D. during this report period

### Agency Support:

Navy N0017-67-A-0044  
NSF GH-31999  
AROD DAHC04-75-G-0156  
ARL F33615-75-C-1084  
ARPA DAA-B07-75-C-1344  
Energy Institute (Stanford)  
Air Force (Wright-Patterson AFB) through SRI - 14111  
NSF/MRL through CMR

### Technical Objective:

Research effort in the ion implantation group at Stanford is presently centered around four major topics: ion implantation and proton-enhanced diffusion in elemental and III-V compound semiconductors; improved computations of range and damage statistics for implanted ions; and ion implantation in CdTe.

### Research Report:

#### (1) Ion Implantation in Transparent Conducting Oxides

Graduate Student: Arnon Gat

The objective of this research is to determine the degree

to which ion implantation can be used to control the optical and electrical properties of transparent conducting oxides. We are particularly interested in the possibility of converting a uniform film of material (such as a sputtered film of  $\text{In}_2\text{O}_3/\text{SnO}_2$ ) into a layered material in which the index of refraction changes with depth. Such a material would be very useful for the preparation of anti-reflection coatings on solar cells and other optical devices.

Results: This is a new project. Sputtered layers have been evaluated and found to be suitable for the work that we wish to do. An annealing furnace has been built to enable us to anneal the implanted material in either oxygen or argon over a temperature range from 200-900°C. Computer programs for the range statistics of ions we wish to implant have been run.

(2) Fabrication of Silicon Solar Cells with Extended Drift Fields

Graduate Student: Frederick C. Wu

Objective: This project is concerned with the development of solar cells in which the cell efficiency is relatively insensitive to defects in the parent material. The approach involves the use of an extended electric field in the body of the solar cell, the electric field being sufficiently large so that photogenerated carriers can be collected efficiently despite low carrier lifetime in the material.

Results: The most important result of this work to date is that cells have been fabricated which show a change in efficiency of less than 10% when the cell is subjected to a dose of  $10^{15}$  1 MeV electrons/cm<sup>2</sup>. Conventional cells show a degradation of approximately 40% under these same conditions. On the basis of this work it appears to be possible to fabricate cells with an end-of-life efficiency (defined as 5 years for a satellite in a synchronous earth orbit) of at least 12%. The work is also of interest for terrestrial cells because low cost materials will tend to be defect-rich and hence cells that have high efficiencies in the presence of defects must be fabricated.

(3) Project: Ion Implantation in Multilayered Media

Graduate Student: David H. Smith

Objectives: The objective of this work is to develop a procedure for calculating range and damage profiles for ions implanted into multilayered targets.

Results: The linearized Boltzmann Equation is used to describe the interaction of an incident ion with the target atoms. This approach allows direct calculation of the ion range profiles and of the behavior of recoiling target atoms resulting from the collisions. A computer program has been written to solve for the ion and recoil atom range distributions for cases in which the incident ion is heavy in comparison to the target atoms (so that angular scattering of the incident ion can be neglected). Experiments are in progress to check the predicted recoil atom distribution when As is implanted through a  $\text{Si}_3\text{N}_4\text{-SiO}_2$  film into a Si substrate. The approach is also being extended to cover the case where large angle scattering of the incident ion must be taken into account.

(4) Project: Process Model for the Annealing of Ion Implanted Boron in Silicon

Graduate Student: Alejandro Chu

Objective: The purpose of this research is to develop a model from which the impurity distribution of ion implanted B in Si can be calculated during the course of annealing. The model must account for the enhanced diffusion which occurs in the implantation-damaged target and for various precipitation and solubility effects that are known to accompany the ion implantation process.

Results: A "diffusion solver" for multiply-interacting species has been implemented on the Stanford IBM 360 computer. The diffusion solver has been used to calculate annealed impurity profiles for B in Si at  $800^\circ\text{C}$ ,  $900^\circ\text{C}$  and  $1000^\circ\text{C}$  for B doses of  $10^{14}$ ,  $10^{15}$  and  $10^{16}/\text{cm}^2$ . Cases adequately covered by our present model, which includes three interacting species, are  $900^\circ\text{C}$  and  $1000^\circ\text{C}$  annealing of layers implanted with  $10^{14}$  and  $10^{15}/\text{cm}^2$ . From an applications standpoint, these are the

most important cases under consideration. However, the model is being developed to include precipitation of B on dislocation loops produced by the implantation, and this feature is required to account for the observed behavior at lower anneal temperatures and higher doses. In effect a four species model is required and is presently being developed and implemented.

(5) Project: Use of Ion Implantation for the Preparation of Halogen-Doped Oxides on Si Substrates

Graduate Student: Thomas Herman

Objective: The purpose of this research is to determine whether halogen-doped oxides can be prepared by the normal thermal oxidation of Cl-implanted Si. This would be an interesting alternative to the present technique in which HCl is introduced into the oxidizing ambient to produce Cl-doped oxides. The oxides themselves are of interest because they show much less sensitivity to mobile ion drift than conventional oxides.

Results: This is a new project. Cl has been introduced into Si by ion implantation after which the Si has been oxidized in a conventional oxidizing system. Initial results suggest that oxides prepared in this way may be as good as those prepared using HCl in the oxidizing ambient insofar as surface state density is concerned. Experiments to verify this initial result and extend it in a number of directions are underway.

(6) Ion Implantation and Annealing of S in GaAs

Graduate Student: Elie Ammar

Objective: The purpose of this project is to determine the conditions under which S can be implanted and annealed in GaAs so as to produce the maximum possible electrical activity.

Results: S and S+B implants into heated ( $300^{\circ}\text{C}$ ) GaAs substrates have been performed at 60 keV. The implanted layers have been encapsulated with  $\text{Si}_3\text{N}_4$ ,  $\text{Ga}:\text{SiO}_2$ , or  $\text{Ga}_2\text{S}_3$  and annealed at a variety of temperatures in the range from  $700^{\circ}\text{C}$  to  $900^{\circ}\text{C}$ . The results suggest that S

is lost in appreciable amounts into both the  $\text{Si}_3\text{N}_4$  and the  $\text{Ga:SiO}_2$  caps, whereas no loss of S is observed when a  $\text{Ga}_2\text{S}_3$  cap is used. Electrical activity of the implanted layers is 25% for a dose of  $10^{14}$  S/cm<sup>2</sup>, which corresponds precisely to the electrical activity expected from the Fermi degeneracy limit. Auger and TEM analyses are underway to determine the structural characteristics of the material after annealing with the various encapsulants. The use of  $\text{Ga}_2\text{S}_3$  may represent an important contribution in the use of ion implantation for doping GaAs.

(7) Project: Use of Ion Implantation to Study the Diffusion Mechanism for n-type Dopants in GaAs

Graduate Student: Alex Lidow

Objective: A variety of explanations are offered in the literature to explain the diffusion behavior of S, Se and Te in GaAs. The purpose of this research is to study the effects which are obtainable when Ga and/or As are co-implanted with the n-type impurity. Implantation of host species will permit us to verify or reject various predictions of currently available models and thus develop an appropriate model and mechanism for the diffusion process under investigation.

Results: Effort has so far been concentrated on the co-implantation of Se and either Ga or As. Implantations have been performed into both Cr-doped substrates and lightly doped LPE layers grown on Cr-doped substrates. The most important results obtained so far are that the electrical activity of the implanted Se can be enhanced significantly by the co-implantation of Ga. Differential sheet resistivity and Hall effect measurements show that the mobility in the implanted layer is a maximum at the point where the Ga concentration is predicted to be equal to the Se concentration. This result is consistent with the theory that electrical inactivity results from the formation of a  $\text{Se-V}_{\text{Ga}}$  complex. So far the effect of this complex on the diffusion of Se has not been clearly identified.



## LIST OF PUBLICATIONS

1. A New Model for Boron Diffusion in Silicon, J. R. Anderson and J. F. Gibbons (to appear February 15, 1976 issue Appl. Phys. Lett.)
2. Measurement of Boron Diffusion in Silicon Using PED, J. R. Anderson and J. F. Gibbons (Appl. Phys. Lett., in press).
3.  $H^+$ - and  $H_2^+$ -Enhanced Diffusion Experiment of S in GaAs, S. Asai, R. E. Tremain, and J. F. Gibbons (Submitted to JAP - March, 1976).
4. Control of Zinc Diffusivity in  $GaAs_{0.6}P_{0.4}$  by Multiple Implantation, E. B. Stoneham and J. F. Gibbons (Submitted to JAP - March, 1976).
5. Mos Measurement of Oxygen Recoils from As Implantation into Silicon Dioxide, A. Goetzberger, D. J. Bartelink, J. P. McVittie, and J. F. Gibbons (Appl. Phys. Lett., in press).

## 26. MÖSSBAUER EFFECT AND RELATED PHENOMENA

S. S. Hanna, Professor, Physics

B. B. Triplett, Assistant Professor, Physics

### Professional Associates:

P. Boolchand <sup>†</sup>	T. Minamisono
E. Bucher*	D. Ramsay
H. C. Jain	T. K. Saylor
G. Langouche**	

<sup>†</sup>Contributor from University of Cincinnati

\*Contributor from Bell Laboratories

\*\*Fulbright Fellow on Leave from University of Leuven, Belgium

### Graduate Students:

N. S. Dixon	W. A. Little	D. G. Mavis
J. W. Hugg*	Y. A. Mahmud	J. H. Stanley
S. M. Lazarus	J. R. Hall	

\*Received MS during report period

### Agency Support:

NSF GP 37106 A1  
NSF MPS 73-08491 A02

Undergraduate Student: T. R. Roelling

### Technical Objective:

To use the Mössbauer effect and perturbed angular correlations to study solid state, atomic, and nuclear phenomena; in particular hyperfine interactions, ion implantation phenomena, atomic interactions in solids and nuclear moments and polarizations.

### Approach:

Nuclear moments of very short lived states are measured by use of hyperfine fields in atoms and ions. New techniques for the measurement of long lived states are being used. Polarized targets are produced by low temperature orientation techniques for studies in nuclear physics. Solid state phenomena are being investigated with the Mössbauer effect at very low temperatures by means of a dilution refrigerator. The structure of amorphous compounds and electronic densities at the nucleus in crystals are also being studied by means of Mössbauer measurements.

Research Report:

(1) Measurement of the Magnetic Dipole Moment of  $^{39}\text{Ca}$  by Use of a Polarized Beam and NMR Detection.

Graduate Students: J.W. Hugg, D.G. Mavis

A measurement of the magnetic moment of  $^{39}\text{Ca}$  has been made, and further progress in the development of the technique for measuring magnetic dipole and electric quadrupole moments is described.

The  $^{39}\text{Ca}$  nuclei ( $I^\pi = 3/2^+$ ,  $T_{1/2} = 0.87$  sec) were produced and polarized by initiating the reaction  $^{39}\text{K}(p,n)^{39}\text{Ca}$  with vector polarized protons ( $P_z = 0.65$ ) from the Stanford FN tandem Van de Graaff accelerator. Initially, a thick polycrystalline target of  $\text{KCaBr}_3$  was used to produce a counting rate of  $\sim 500$  cps for an incident beam intensity of only 10 nA. The proton polarization was transverse to the beam direction and a 6.5 kG holding field was applied parallel to the polarization direction. The  $\beta$ -particles from the  $^{39}\text{Ca}$  decay were detected by two particle telescopes placed at  $0^\circ$  and  $180^\circ$  to the polarization direction. The  $\text{KCaBr}_3$  target was exposed to the proton beam for 1.2 sec every 2.4 sec and  $\beta$ -particles were counted only with the beam off. The proton polarization was reversed (by RF transitions in the polarized ion source) on alternate cycles, so that the absolute  $\beta$ -particle asymmetry was determined independent of instrumental asymmetries.

Following the preliminary work with  $\text{KCaBr}_3$ , targets of  $\text{KCaI}_3$  and  $\text{KBr}$  were used. In each case a holding field  $H_0$  of 6.5 kG was employed. It was found that the  $\beta$ -asymmetries depended very much on the samples, while the spin-lattice relaxation time was about 3 sec in all samples. These values of  $T_1$  are considerably longer than the nuclear lifetimes, so that polarization and nuclear moment measurements can be readily carried out. We interpret the resonance in  $\text{KBr}$  as showing that many  $^{39}\text{Ca}$  ions are implanted in K substitutional sites in the cubic crystal and these ions are doubly ionized in these sites. The NMR linewidth is very narrow,  $\text{FWHM} = 3.0(7)$  kHz, and the asymmetry is completely destroyed at the center of the resonance; this observation supports the assumption of equivalent stable cubic sites for the  $^{39}\text{Ca}$  ions. The NMR resonances in  $\text{KCaBr}_3$  and  $\text{KCaI}_3$  had linewidths (FWHM) of  $1.5 \times 10^2$  kHz, as expected from the crystal structure and polycrystalline character of the samples used. The values of the magnetic moment determined in

these samples are less precise but agree with the value determined in KBr. The uncorrected value from the resonance in KBr is  $\mu = 1.02015(12)$  nm. After applying the diamagnetic correction  $\sigma = 1.45(10)^{-1}$  the corrected magnetic moment is

$$\mu(^{39}\text{Ca}) = 1.0216(2) \text{ nm.}$$

The sum of the magnetic moments of mirror states is known to be independent of mesonic effects and also of configuration mixing for any central interaction.<sup>2</sup> Furthermore, the observed sum is usually close to the sum of the Schmidt values. For  $^{39}\text{Ca}$  and  $^{39}\text{K}$  the observed sum is 1.41 nm, whereas the sum of the Schmidt values is 1.27 nm. The quite large deviation of +0.14 nm increases to 0.18 nm when the relativistic effect<sup>3</sup> on the nuclear moment is taken into account.

(2) Decoupling of the Hyperfine Interactions in  $^{16}\text{O}$  Ions Recoiling in Vacuum.

Graduate Students: A. Little, S.M. Lazarus.

Magnetic hyperfine interactions in highly stripped light ions produced in nuclear reactions have been studied through perturbed angular correlations following recoil into vacuum in the presence of large external axial magnetic fields. The second excited state of  $^{16}\text{O}$  ( $I^\pi = 3^-$ ,  $E = 6.13$  MeV,  $\tau = 26.6$  psec,  $g = 0.55$ ) was studied by use of the  $^{19}\text{F}(p,\alpha)^{16}\text{O}^*$  reaction at bombarding energies of 0.874, 1.374, and 2.026 MeV, and the  $^{16}\text{O}(\alpha,\alpha')^{16}\text{O}^*$  reaction at 17.55 MeV. In the latter case two measurements were made, one with the recoils allowed to pass directly into vacuum and a second with the recoils passing first through a foil so as to reduce their velocity. Five recoil velocities between 1.0 and 3.3%  $c$  were thus obtained, which produced average ionic charge states varying from 1.8 to 5.5. The 6.13-MeV gamma ray de-exciting the  $3^-$  state was observed in coincidence with alpha particles emitted at  $180^\circ$ , giving rise to a large anisotropy in the angular correlation. The anisotropy was observed as a function of an external axial magnetic field from zero to 33 kG. The unperturbed angular correlation was also measured following recoil into a suitable solid backing.

The perturbation of the nuclear angular correlation is expected to arise primarily from unpaired 1s and 2s electrons in oxygen, as higher-lying electrons are expected to produce hyperfine fields too weak to perturb the nucleus appreciably during its lifetime. A study of atomic transition rates suggests that the interactions are primarily static in nature, as transitions to the K and L shell (when allowed) occur in a time much shorter than the nuclear lifetime, whereas those within the L shell require a much longer time. The hyperfine fields have been calculated by a Hartree-Fock-Slater approach. The external field, when sufficiently strong, is expected to decouple the hyperfine interaction of the 2s electrons, thereby preserving the unperturbed nuclear angular correlation in ions not containing unpaired 1s electrons. The experimental data have been fit with a static statistical model in which the 1s shell is assumed to be fully occupied if two or more electrons are present, and the remaining electrons are assumed to be distributed statistically among the 2s and 2p orbitals. Higher orbitals have also been considered. From these fits, the nuclear g-factor and the fraction of nuclei experiencing perturbation have been extracted. The g-factor is consistent with results of other methods; the fraction of nuclei experiencing perturbation is, however, found to be smaller than predicted by the statistical model. This suggests that the L-shell electrons may not be statistically distributed. Further details of the experiment may be found in the thesis of A. Little.

(3) Magnetic Hyperfine Structures of  $^{125}\text{Te}$   
in Ferromagnetic  $\text{Pd}_2\text{MnSb}$

A clear magnetic hyperfine structure for  $^{125}\text{Te}$  has been observed in the cubic ferromagnetic Heusler alloy  $\text{Pd}_2\text{MnSb}$  in a Mössbauer effect experiment. Although such a structure has been observed previously in other hosts, the internal field in the present experiment  $H_{\text{int}} = +187 \pm 9 \text{ kOe}$  at 4.2 K is to our knowledge the largest yet seen at the Te nucleus. This measurement has a twofold significance. First, the occurrence of a large  $H_{\text{int}}$  has resulted in a precise measurement of the nuclear  $g$  factor ratio  $g_e/g_o = -0.2270 \pm 0.0015$ . Combining this result with the known ground state  $g$  factor,  $g_o = -1.77666 \pm 0.00006$ , one obtains the excited state  $g$  factor  $g_e = +0.4033 \pm 0.0026$ . By adopting this value of  $g_e$ , partially resolved  $^{125}\text{Te}$  magnetic hyperfine spectra can be analyzed to yield more precise internal field values than hitherto possible. Second, internal fields at non-magnetic sites (X and Y) in ferromagnetic Heusler alloys ( $\text{X}_2\text{MnY}$ ) have recently been the focus of attention both experimentally and theoretically. The magnitude of the  $\text{Sn}^4$  and  $\text{Sb}^5$  fields in  $\text{Pd}_2\text{MnSb}$  have been measured by use of the Mössbauer effect and the  $\text{Cd}^6$  field in the same host by means of perturbed angular correlations. Combining these results with the present measurement on Te, one observes a systematic increase in the magnitude of the fields as a function of the number of outer electrons of the "5sp" impurity. This dominant feature of the internal fields in Heusler alloys is quite similar to that in Fe metal.

Samples of  $\text{Pd}_2\text{MnSb}$  were prepared from 99.9% pure Pd and Mn and 99.999% pure Sb by induction melting the elements in an argon

atmosphere. X-ray examination of the samples showed a cubic phase with a lattice constant  $a_0 = 6.423 \pm 0.005 \text{ \AA}$ , in good agreement with earlier reports. A 3 mC quantity of radioactive  $^{125}\text{Sb}$  was electroplated onto a  $\text{Pd}_2\text{MnSb}$  platelet (ca. 1 mm thick) and diffused into the sample by heating to  $1000^\circ\text{C}$  in vacuum for approximately 2 days. Zero field spectrum yielded  $H_{\text{int}}$  and  $g_e/g_0$ . A weak line near zero velocity was observed in all the spectra and was included in the fitting procedure. The enhancement of the  $\Delta m = 0$  magnetic components in zero applied field indicates partial magnetization of the source in the plane of the platelet. The absence of a measurable quadrupole interaction is consistent with the cubic nature of the source matrix. At 78 K the internal field value was found to be  $819 \pm 12 \text{ kOe}$ . This value of  $H_{\text{int}}$  represents a 4.4% reduction from its value at 4.2 K and thus it appears to scale with the host magnetization.

The positive sign of the Te field in  $\text{Pd}_2\text{MnSb}$  was established from measurements on the  $^{125}\text{Sb}$  source placed in a magnetic field produced by a superconducting solenoid. In the longitudinal geometry employed ( $\gamma$  rays detected parallel to the applied field) the linearly polarized  $\Delta m = 0$  lines of the spectrum were suppressed in an applied field of 52 kOe and nearly so in a field of 13 kOe. The sign of the hyperfine field is uniquely determined from the spectra in two ways. First, the line positions are observed to shift to larger velocity in the field of 52 kOe, indicating that the hyperfine field is parallel to the magnetization. However, although the experimental result is clearly established, there might be some subtle magnetic effect in these alloys that could mask the true result. Second, the ZnTe absorber was located at a point on the solenoid axis where it was exposed to about 50% of the field applied to the source. Such a "split-split" combination of source and absorber results in an 8 line magnetic spectrum which appears as four unresolved doublets. Because of the Zeeman polarizations in the source and absorber, the effective shifts of these doublets are non-linear, such that the weak inner lines show a relatively

larger shift with applied field than the outer lines. Since this effect involves the non-magnetic absorber, the excellent fit to the data with a positive hyperfine field at Te in  $\text{Pd}_2\text{MnSb}$  establishes the sign of this field.

(4) Nuclear Orientation Effects in  $^{125}\text{Te}$  ( $\text{Pd}_2\text{MnSb}$ ) Mossbauer Spectra.

Graduate Students: N.S. Dixon  
Y. Mahmud

Nuclear polarization effects in magnetically split  $^{125}\text{Te}$  Mossbauer spectra were observed at very low temperatures. A 3 mC source of  $^{125}\text{Sb}$  diffused into  $\text{Pd}_2\text{MnSb}$  was attached to the mixing chamber of a  $^3\text{He}$ - $^4\text{He}$  dilution refrigerator with Cd-Bi solder. Radioactive heating generally prevents sources attached in this manner from reaching the temperature of the mixing chamber. A nuclear thermometer was therefore placed in intimate thermal contact with the  $^{125}\text{Sb}$  source: a weak  $^{57}\text{Co}$  source, diffused into a Fe foil, was Cd-Bi soldered on top of the  $^{125}\text{Sb}$  source, and a Mossbauer spectrum was recorded. From the asymmetry in this spectrum a temperature of  $139^{+19}_{-15}$  mK could be deduced, considerably higher than the mixing chamber temperature.

The  $^{125}\text{Sb}$  ground state decays partly to the isomeric state of  $^{125}\text{Te}$ . About 26 percent of the feeding of the excited Mossbauer level comes directly from this ( $T_{1/2}=58$  days) state, while the remaining feeding of the Mossbauer level comes from the  $^{125}\text{Sb}$  ground state via very short-lived intermediate higher excited states of  $^{125}\text{Te}$ . As a consequence of this the asymmetry observed in the  $^{125}\text{Te}$  spectrum is due to the nuclear orientation of both the  $^{125}\text{Sb}$  ground state and the  $^{125\text{m}}\text{Te}$  state, as the latter one reorients completely during its long lifetime.

As experimental values are available for  $|\mu|$  and  $|H|$  at the  $^{125}\text{Sb}$  ground state <sup>7,8</sup>,  $|\mu|$  and  $H$  at the  $^{125\text{m}}\text{Te}$  state <sup>9, 10</sup>, and for the multiplicities of the intermediate transitions <sup>11</sup>, it can be shown that the  $^{125}\text{Sb}$  polarization will have the largest influence on the Mossbauer spectrum asymmetry. Therefore, the direction of the asymmetry indicates a positive sign of  $|\mu|$  at the  $^{125}\text{Sb}$  ground state.



The magnitude of the observed asymmetry, on the other hand, indicates that the polarized  $^{125}\text{Te}$  state tends to produce an asymmetry in the opposite direction, indicating a negative sign of  $\mu\text{H}$  in the  $^{125\text{m}}\text{Te}$  state.

Since we measured a positive sign for  $\text{H}(\text{Te})$  [see (3)], we conclude that the  $^{125\text{m}}\text{Te}$  magnetic moment is negative. We cannot compare this sign to other  $11/2$  isomeric states in odd  $\text{Te}$  isotopes, since none of the signs have been measured. However, the similar  $11/2$  isomeric states in  $^{113}\text{Sn}$  and  $^{119}\text{Sn}$  also have a negative magnetic moment. The isomeric  $11/2$  states in these isotopes are expected to have negative magnetic moments, from calculations<sup>12</sup> based on the so-called "pairing plus quadrupole" model.

If we assume  $\text{H}(\text{Sb})$  to be positive, as expected from the sign at the  $\text{Te}$  nuclei, this would result in a positive sign for the  $^{125}\text{Sb}$  ground state magnetic moment, in good agreement with the sign of the similar  $^{123}\text{Sb}$  ground state moment, and with predictions by L.S. Kisslinger and R.A. Sorensen<sup>12</sup>.

#### (5) Magnetic Hyperfine Structure in Mixed-Valence-State Compound $\text{TmSe}$ .

Graduate Student: N.S. Dixon

The concept of rapid valence fluctuations between two distinctly different  $4f$  electronic configurations has been advanced as an explanation for the demagnetization of rare earth (RE) ions in certain dilute alloys and some intermetallic compounds. This proposal remains quite controversial and alternative mixing and hybridization schemes have been advanced to avoid the concept of real-time fluctuations.

The occurrence of an anomaly in the low temperature susceptibility of  $\text{TmSe}$  suggested the possibility of magnetic ordering in this mixed valence state material. We have performed a careful study of magnetic hyperfine structure detected "non-destructively" utilizing the Mössbauer effect. The spectra obtained have now been completely analyzed and provide a rather clear picture of the magnetic and valence structure of this simple cubic material at our measuring time of  $\sim 1.0^{-9}$  sec.

First, the spectra all show well identified 6 line magnetic hyperfine structures below the suspected ordering temperature,  $T_c = 2.85^\circ \text{K}$ . The nuclear polarization observed in the spectra

taken near  $0.05^\circ \text{K}$  is consistent with the measured temperatures and the observed value of  $\langle H_{\text{eff}} \rangle$ , the average hyperfine field. This observation leaves no doubt that  $\text{TmSe}$  is magnetically ordered on our experimental timescale (It is conceivable that this magnetic order is not "long range" in the usual sense of the word since magnetic clusters fluctuating on time scales substantially slower than  $10^{-9}$  sec could also produce the observed result).

Second, the small quadrupole interactions observed in the spectra are consistent only with cubic charge symmetry and the associated cubic crystalline electric field. For instance, such small quadrupole interactions are not consistent with a random mixture of divalent and trivalent  $\text{Tm}$  ions in the material (see the following section for a discussion of the material  $\text{TmSe}_{1.1}$  which has very strongly noncubic charge symmetry in spite of a lattice structure which would be conventionally labeled simple cubic).

Third, this spectrum has been decomposed into three distinct 6 line structures associated with the  $\text{Tm}^{3+}$  and the  $\text{Tm}^{2+}$  ground electronic states and the  $\text{Tm}^{2+}$  first excited electronic state which still has a significant population. The hyperfine properties of the structures were compared with a molecular field-point charge description of the  $\text{Tm}$  valence states. If one parameter (either the  $\text{Tm}^{2+}$  or  $\text{Tm}^{3+}$  ground state hyperfine field) is fitted to the data, all other parameters are in principle determined by the theory. The predicted parameters include hyperfine fields (or magnetic moments) of the other ground state and the  $\text{Tm}^{2+}$  excited state, the quadrupole interaction of all three states, and the population of the  $\text{Tm}^{2+}$  excited state. Quite satisfactory agreement with theory is obtained considering the known limitations of the model and incomplete information on second-order effects, in particular, a small and difficult to measure distortion from perfectly cubic symmetry which occurs as a result of magnetostriction below the ordering temperature. Quantitative

agreement between the theoretical description and the measured hyperfine parameters can be obtained if we let this distortion be a variable of the description.

Fourth, a most important result from these measurements is that no relaxation effects which might be associated with fluctuations between the  $Tm^{3+}$  and  $Tm^{2+}$  states appear in the the composite spectrum. The absence of such effects means that any fluctuations must occur more slowly than  $10^{-9}$  sec. This is the opposite behavior from that observed for SmS. Similarly, any "thermal reservoir" associated with such fluctuation is limited to  $T_{ICF} \lesssim 0.020^\circ K$  and would be insufficient to inhibit magnetic ordering in this material.

Thus, we have observed a mixed valence material which behaves very differently than many such materials. The suggestion is that the characteristic mixing time  $\tau_{ICF}$  can have enormously different values in different mixed valence state materials.

Lastly, it is important to tie together the ramifications of the second and fourth points above. In spite of the fact that both valence states are observed, there is no suggestion of the very large and very different quadrupole interactions that are expected to appear in components of the spectrum in the event of noncubic electric charge distributions. A rather simple possible explanation for this phenomenon can still be consistent with real-time fluctuations, namely, that the electron jumping on or off the 4f electronic level is sufficiently localized so that (say in the  $Tm$  d-band) the  $Tm$  ion produces nearly the same effective charge regardless of whether it is in the "divalent" or "trivalent" state.

We are actively expanding the scope of our mixed valence state program and intend to start measurements in external magnetic fields shortly.

(6) Vacancy Induced Hyperfine Structure in the  
Nonstoichiometric Compound  $\text{TmSe}_{1.1}$

Graduate Student: N.S Dixon

Intermetallic compounds with stoichiometry  $\text{TmSe}_x$  can be prepared with the cubic NaCl crystal structure for values of  $x$  ranging from about 0.95 to 1.2. Although the structure of the materials formed for  $x \neq 1.0$  cannot be strictly NaCl structure, they certainly have predominantly cubic symmetry. Thus the question arises: "Where do the excess Se or Tm ions sit in the predominantly NaCl lattice of these nonstoichiometric materials?".

Mössbauer spectra were taken with an absorber ( $8 \text{ mg/cm}^2$  of  $^{169}\text{Tm}$ ) prepared from a powdered single crystal of  $\text{TmSe}_{1.1}$  with lattice constant  $a_0 = 5.624(2) \text{ \AA}$ . The sample shows a sharp magnetic susceptibility kink at 4.2 K characteristic of magnetic ordering and spectra taken in the paramagnetic region above this temperature show a large quadrupole splitting and characterize the crystalline electric field symmetry as lower than cubic. **Relaxation effects** in the paramagnetic hyperfine structure appear as an increasing asymmetry in the quadrupole-split spectrum as  $T$  approaches  $T_c$ . The effect shows that at least two magnetic electronic levels must be at 5.46 K and suggests that the crystalline electric field (CEF) ground state in this material is a magnetic doublet. Careful studies of the temperature dependence of the quadrupole interaction will give detailed information on the strength and symmetry of the CEF interaction and the resulting electronic wavefunction.

A spectrum taken at 0.060 K shows the full free ion hyperfine parameters for the  $\text{Tm}^{3+}$  ion ( $\approx 7.1 \text{ MOe}$  hyperfine field and  $\approx 15 \text{ cm/sec}$  quadrupole splitting). Spectra at higher temperatures show a distinct similarity with features in the spectra previously observed in Tm metal which have been attributed to the development of a sinusoidal spatial variation of magnetic moments. Such a behavior is consistent with neutron

diffraction studies of Tm metal. Indeed, the  $\text{TmSe}_{1.1}$  spectra are so strikingly similar to the spectra taken on Tm metal at higher temperatures that we propose that such a spatial variation of moments occurs in this material as well.

It has been proposed that the crystalline and magnetic properties of such cubic nonstoichiometric materials can be understood in terms of a complete simple cubic anion sublattice and a cation sublattice containing vacancies. Let us consider such a model for  $\text{TmSe}_{1.1}$  and note that the stoichiometry implies that a given Tm site will have approximately one vacancy among its 12 Tm nearest neighbor (nn) sites in the Tm sublattice. Such a single vacancy will produce a large CEF at the Tm absorber site and lead to electronic wavefunctions with large quadrupole interactions as well as larger magnetic moments in the event that magnetic order develops. Indeed, a maximum in the ordering temperature  $T_c$  occurs in the  $\text{TmSe}_x$  materials at the composition  $x=1.1$ . We believe this maximum in  $T_c$  and the sharpness of the transition is associated with the fact that there is generally only a single vacancy in the near neighbor cation shell surrounding a given Tm site.

It is appropriate to consider the question of whether these vacancies exist in an ordered array or not. Consider the possibility that the distribution of vacancies is random: some  $\text{Tm}^{3+}$  cations will then be surrounded by nn shells containing no vacancies as well as 1, 2, 3, or more vacancies. Specifically, if  $P(y)$  is the probability that a given  $\text{Tm}^{3+}$  site is surrounded by a nn shell containing  $y$  vacancies then  $P(y) = 0.323, 0.383, 0.208, 0.069, \text{ and } 0.015$  for  $y = 0, 1, 2, 3, \text{ and } 4$ , for a random vacancy distribution. Thus, 32% of the Tm sites should have predominantly cubic symmetry and an associated hyperfine field considerably less than the free ion value. There is no evidence for such a large percentage of cubic sites in the  $\text{TmSe}_{1.1}$  spectrum taken at 0.060 K. This observation, coupled with the sharpness of the magnetic susceptibility kink, and the evidence for a

sinusoidal spatial variation of magnetic moments at higher temperatures, implies fairly long range order in the vacancy sublattice and suggests experiments to search for this order, namely, careful x-ray and neutron diffraction work on a single crystal of  $\text{TmSe}_{1.1}$ .

Additional studies of this material with the Mössbauer effect are continuing.

(7) High Temperature Mössbauer Studies of  $\text{TmVO}_4$ ,  $\text{TmAsO}_4$ , and  $\text{TmPO}_4$ .

Graduate Student: N.S. Dixon

Preliminary high temperature Mössbauer studies have been conducted on  $\text{TmVO}_4$ ,  $\text{TmAsO}_4$ , and  $\text{TmPO}_4$  in the temperature range 300 K to 1000 K.

The quadrupole splitting may be written:

$$\langle \Delta E \rangle_T = (1/2) \rho_1 \langle 3J_Z^2 - J^2 \rangle_T + \rho_2 C_2^0$$

where the first term represents the electronic contribution and the second represents the lattice contribution. At temperatures much greater than the crystalline electric field (CEF) splitting of the ground multiplet, the temperature average  $\langle 3J_Z^2 - J^2 \rangle_T$  in the electronic term is proportional to  $1/T$  in first order, and thus at high temperature the lattice term can be separated from the electronic contribution.

Our preliminary measurements have thus yielded perhaps the most effective separation of these terms to date, and give tentative values for  $|\rho_2 C_2^0|$  of  $\{2.0 \pm 0.2 \text{ cm/s; } 5.6 \pm 0.6 \times 10^{-7} \text{ eV}\}$ ,  $\{1.2 \pm 0.4 \text{ cm/s; } 3.4 \pm 1.0 \times 10^{-7} \text{ eV}\}$ , and  $\{1.4 \pm 0.2 \text{ cm/s; } 3.9 \pm 0.6 \times 10^{-7} \text{ eV}\}$  respectively for  $\text{TmVO}_4$ ,  $\text{TmAsO}_4$ , and  $\text{TmPO}_4$ . These rather different values for the lattice terms in  $\text{TmVO}_4$  and  $\text{TmAsO}_4$  may explain their difference in quadrupole splittings at low temperature (but above the

Jahn-Teller distortion) despite their very similar ground state wave functions; but of course they raise the question: "Why are the lattice terms so different?".

We intend to explore this question with more careful studies and the following experimental improvements. First, the copper absorber mount in the furnace has been replaced by a niobium mount to prevent coating the absorber and beryllium windows with copper at the highest temperatures. Second, carbon filler in the absorbers tends to decompose the thulium compounds; we therefore intend to use quartz powder or  $\text{Al}_2\text{O}_3$  as filler in our further studies.

(8) Structure of the Amorphous Phases of Se and Te

Graduate Student: Y. Mahmud

The Mössbauer effect (ME) in  $^{125}\text{Te}$  has been used to study the structure of the amorphous phases of selenium and tellurium. Absorbers were prepared from amorphous,  $\alpha$ -monoclinic and trigonal samples of selenium containing 1.8 atom %  $^{125}\text{Te}$ . Sputtered films of  $\text{a-Ge}_y\text{Te}$  were prepared with different concentrations  $y$ , and ME parameters were then measured as a function of the concentration  $y$ . The quadrupole splitting for  $\text{a-Ge}_y\text{Te}$  was found to be a linear function of  $y$  for  $0.05 \leq y \leq 0.33$ . This behavior is consistent with either the two-site or three-site model originally proposed by Boolchand. Consequently, extrapolation to  $y = 0$  is expected to yield the quadrupole splitting of  $\text{a-Te}$ .

Recently, a ME study of  $\text{Te}$  vapor isolated in noble gas matrices has been reported. The ME absorption spectra, attributed to the  $\text{Te}_2$  dimer, yield values of the quadrupole splitting and isomer shift which are identical with our values for  $\text{a-Te}$  (see table 1). The major contribution to both measured parameters comes from the electronic structure of the  $\text{Te}$  atom in  $\text{Te}_2$  and  $\text{a-Te}$ ; thus, we conclude that these electronic structures are identical. We are exploring the consequences of this result and

the possibility that the ground state electronic structure of the  $\text{Te}_2$  molecule is either known or can be calculated from first principles.

The quadrupole splitting of  $\alpha$ -Te is about 24% larger than that of  $t$ -Te, while the quadrupole splittings of  $\alpha$ -Se and  $\alpha$ -monoclinic Se are about 16% larger than that of  $t$ -Se. In another recent development, Martin and Lucovsky noted that a deformation parameter can be assigned to the progression of Group VI elements going from molecular sulfur to metallic simple cubic polonium. The deformation parameter  $R/r$ , where  $R$  is the inter-chain distance and  $r$  is the bond length, decreases from 1.7 for molecular S to 1.0 for cubic Po. Martin and Lucovsky also noted that the ratio of two optical frequencies associated with the force constants of the materials in question scale with the deformation parameter  $R/r$ . These two frequencies must be degenerate in the cubic limit  $R/r = 1$ , where the quadrupole splitting (QS) in the ME spectra must also vanish. Therefore, we have related QS to  $R/r$  and observe a similar correlation. The linearity is surely fortuitous since QS must vanish at  $R/r = 1$ , while an extrapolation of the observed relation indicates an intercept of approximately 6 mm/sec. Nevertheless, if we assume some validity of the existing relation between  $\sim 8$  mm/sec and  $\sim 12$  mm/sec we can turn the argument around and ask if the observed QS for a material with unknown  $R/r$  is a useful basis for predicting the deformation parameter. For  $\alpha$ -Te, for instance, the QS implies an inter-chain distance of 4.03 Å, close to the second strong peak in the RDF measured by Ichikawa. The bond lengths are concluded to be shorter and the bond angles larger in the amorphous phases than in the trigonal phases of Se and Te.

Finally, we intend to explore the question raised by this result, namely, that the electronic structure in these chain materials seems to be directly related to the deformation parameter which originates from the bonding structure of the materials.



Table 1.

	a-Te	Te <sub>2</sub> in Noble Gas Matrix
Quadrupole splitting (mm/sec)	9.60 ± 0.05	9.60 ± 0.07
Isomer shift (mm/sec)	+0.41 ± 0.06	+0.34 ± 0.07

## REFERENCES

- <sup>1</sup> F. D. Feiok and W. R. Johnson, Phys. Rev. Lett. 21, 785 (1968).
- <sup>2</sup> H. A. Mavromatis and L. Zamick, Phys. Lett. 20, 171 (1966)
- <sup>3</sup> H. Ohtsubo, M. Sano, and M. Morita, J. Phys. Soc. Japan 34 Suppl., 509 (1973)
- <sup>4</sup> C. C. M. Campbell and W. Leiper, Conf on Magnetism and Magnetic Materials, Boston (1973), 319.
- <sup>5</sup> L. J. Swarzendruber and B. J. Evans, Phys. Lett. 38A (1972) 511.
- <sup>6</sup> W. Walus, R. Goss-Zurek, B. Styczen, A. Szytula and J. Styczen, Proc. Int. Conf. on Hyperfine interactions studies in nuclear reactions and decay, Uppsala (1974), 182, and private communication.
- <sup>7</sup> P. T. Callaghan, M. Shott, N.J. Stone, Nucl. Phys. A221, 1 (1974).
- <sup>8</sup> L. J. Swartzendruber, B. J. Evans, Phys. Lett. 38A, 511 (1972).
- <sup>9</sup> R. E. Silverans, R. Coussement, G. Dumont, H. Pattyn, L. Vanneste, Nucl. Phys. A193, 367 (1972).
- <sup>10</sup> P. Boolchand, M. Tenhover, S. Jha, G. Langouche, B. B. Triplett, S. S. Hanna, P. Jena, Phys. Lett. 54A, 293 (1972).
- <sup>11</sup> K. S. Krane, J.R. Sites, W. A. Steyert, Phys. Rev. C4, 565 (1971)
- <sup>12</sup> L. S. Kisslinger, R. A. Sorensen, Rev. Mod. Phys. 35, 853 (1963).

# RECENT PUBLICATIONS

- <sup>1</sup> T. Minamisono, J.W. Hugg, D.G. Mavis, T.K. Saylor, H.F. Glavish, and S. S. Hanna, "Measurement of The Magnetic Moment of <sup>39</sup>Ca by Use of a Polarized Proton Beam and NMR Detection," Phys. Lett. 61B, 155 (1976)
- <sup>2</sup> T. Minamisono, J.W. Hugg, D.G. Mavis, T.K. Saylor, S.M. Lazarus, H.F. Glavish and S. S. Hanna, "Nuclear Moment Determination of  $\beta$ -Emitting Nuclei by Use of Nuclear Reactions Initiated with Fast Polarized Beams," Contributed paper to the International Meeting on Hyperfine Interactions, Leuven, Belgium (1975).
- <sup>3</sup> P. Boolchand, M. Tenhover, S. Jha, G. Langouche, B. B. Triplett, S. S. Hanna, and P. Jena, "Magnetic Hyperfine Structure of <sup>125</sup>Te in Ferromagnetic Pd<sub>2</sub>MnSb," Phys. Lett. 54A, 293 (1975).
- <sup>4</sup> G. Langouche, B. B. Triplett, N.S. Dixon, S. S. Hanna, and P. Boolchand, "Nuclear Orientation of <sup>125</sup>Sb in Pd<sub>2</sub>MnSb Observed with the Mossbauer Effect of <sup>125</sup>Te," Phys. Rev. C (in press).
- <sup>5</sup> H.C. Jain, A. Little, S.M. Lazarus, T.K. Saylor, B. B. Triplett, and S. S. Hanna, "Magnetic Moment of the 3<sup>-</sup> Level of <sup>40</sup>Ca from Magnetic Decoupling in Free Ions", Phys. Rev. C (submitted for publication).
- <sup>6</sup> G. Langouche, N.S. Dixon, Y. Mahmud, B. B. Triplett, S. S. Hanna, and P. Boolchand, "Magnetic Moment of the First Excited State of <sup>121</sup>Sb and the Hyperfine Field in Pd<sub>2</sub>MnSb," Phys. Rev. C (submitted for publication).
- <sup>7</sup> P. Boolchand, M. Tenhover, S. Jha, G. Langouche, B. B. Triplett, and S. S. Hanna, "Magnetic Hyperfine Structure of <sup>119</sup>Sn in Ferromagnetic Pd<sub>2</sub>MnSb," Solid State Communications (submitted for publication).

- <sup>8</sup> T. Minamisono, J.W. Hugg, D.G. Mavis, T.K. Saylor, S.M. Lazarus, H.F. Glavish and S. S. Hanna, "Hyperfine Studies by Use of Polarized Reactions," Proceedings of Fourth International Symposium on Polarization Phenomena in Nuclear Reactions, Zurich, Switzerland (1975).
- <sup>9</sup> T. Minamisono, J.W. Hugg, J.R. Hall, D.G. Mavis, H.F. Glavish and S. S. Hanna, "Measurement of the Magnetic Dipole Moment of  $\beta$ -Emitting <sup>25</sup>Al by Use of a Polarized Proton Beam and NMR Detection," Phys. Rev. C (in press).

## 27. GENERATION OF ULTRAVIOLET AND VACUUM ULTRAVIOLET RADIATION

S. E. Harris, Professor, Electrical Engineering  
J. F. Young, Adjunct Professor, Electrical Engineering

### Professional Associates:

D. M. Bloom

### Graduate Students:

G. W. Bekkers	J. C. White
R. W. Falcone	M. D. Wright
W. R. Green	G. A. Zdasiuk
K. S. Hsu	L. J. Zych
D. B. Lidow*	
J. H. Newton	
E. A. Stappaerts*	

\*Received PhD during report period.

### Agency Support:

AFCRL F19628-75-C-0046  
ARMY DAAG29-74-C-0033  
NAVY N00014-75-C-0576  
ARPA N00014-75-C-1175  
NASA NGL-05-020-103  
ERDA E(04-3)-326, P.A. 41

### Technical Objective:

To develop techniques for producing coherent radiation in the ultraviolet, vacuum ultraviolet, and soft x-ray spectral regions; to study and to develop optically induced inelastic collisions as a means of producing high power lasers, amplifiers, and of stimulating chemical reactions; to investigate the use of resonant charge exchange collisions to produce metastable atomic storage for high energy lasers; and to continue development of our efficient infrared image up-conversion in metal vapors.

## Research Report:

During this year we have demonstrated the first example of a process where a large cross section for atomic inelastic collision is created by applying optical radiation at the frequency corresponding to the energy defect of the levels. Thus energy transfer between two atomic species is initiated or "switched" by the optical signal. We have observed this process in a mixture of Sr and Ca; energy was first stored in the radiatively trapped  $5p^1P^0$  level of Sr I, and then transferred to the  $4d^1D$  level of Ca I using a laser at  $6409 \text{ \AA}$ . At a laser power density of  $8.6 \times 10^6 \text{ W/cm}^2$  about 11% of the excited Sr energy was transferred, implying an induced cross section of  $3 \times 10^{-16} \text{ cm}^2$ .

Theory predicts that the optically induced cross section should continue to increase linearly with power density up to  $9 \times 10^{-14} \text{ cm}^2$ , and large, fast energy transfers should be possible. We believe this will have a number of exciting applications, including construction of short wavelength lasers, and direct measurement of inter-atomic potentials. The inverse radiative process where stimulated emission takes place between an excited state of one species and a lower state of a second species may be applicable to the construction of low gain, high energy lasers. These possibilities, and others, are currently being studied.

We have demonstrated the first infrared image up-conversion in metal vapors. These systems have the advantage of large apertures, and high efficiencies, compared to crystal systems. A Nd:lanthanum beryl-late laser is used to pump the Cs two-photon  $6s-7s$  level, and the infrared image at about  $3 \mu$  is up-converted to  $4560 \text{ \AA}$ . Using 8 kW of laser power, a 2000 resolvable spot image has been up-converted at a power conversion efficiency of 20%. We believe that considerable improvements can still be made, and that these systems will prove useful for astrophysics, for imaging fast events such as fusion pellet implosions, and for IR spectroscopy.

A strong effort to generate very short wavelengths of coherent light continues. We are presently assembling a three frequency sum

generation experiment in neon to produce 625 Å and 426 Å. Such a source could prove extremely valuable for material analysis, photo-ionization studies, and imaging. We are very interested in extending the VUV holography pioneered by us at 1182 Å to shorter wavelength (higher resolution) regions. These wavelengths should be particularly adapted to imaging biological materials.

#### Reference Publications:

1. E. A. Stappaerts, "Harmonic Generation at High Field Strengths, Frequency Shifts and Saturation Phenomena," Phys. Rev. A 11, 1664 (May 1975).
2. D. M. Bloom, G. W. Bekkers, J. F. Young, and S. E. Harris, "Third Harmonic Generation in Phase Matched Alkali Metal Vapors," Appl. Phys. Lett. 26, 687 (June 1975).
3. D. M. Bloom, J. F. Young, and S. E. Harris, "Mixed Metal Vapor Phase Matching for Third Harmonic Generation," Appl. Phys. Lett. 27, 390 (October 1975).
4. K. S. Hsu, A. H. Kung, L. J. Zych, J. F. Young, and S. E. Harris, "1202.8 Å Generation in Hg Using a Parametrically Amplified Dye Laser," IEEE J. Quant. Elect. QE-12, 60 (January 1976).
5. D. B. Lidow, R. W. Falcone, J. F. Young, and S. E. Harris, "Inelastic Collision Induced by Intense Optical Radiation," Phys. Rev. Lett. 36, 462 (March 1976).
6. E. A. Stappaerts, G. W. Bekkers, J. F. Young, and S. E. Harris, "The Effect of Linewidth on the Efficiency of Two-Photon-Pumped Frequency Converters," IEEE J. Quant. Elect. (to be published).

## 28. PSEUDOPOTENTIAL METHODS IN PHYSICS

W. A. Harrison, Professor of Applied Physics

### Graduate Students:

R. J. Sokel

### Agency Support:

NSF GH 39811

Army DAHC04-73-C-0024

Army DAAK02-74-C-0069

NSF DMR 74-22230

### Technical Objectives:

To understand the electronic structure of solids and its relation to the properties of the solid.

### Research Report:

We have expanded our scope to a general reformulation of the bonding properties of solids. Simple covalent solids are understood in terms of bond orbitals and simple metals in terms of pseudopotentials. We have completed a major study of mixed tetrahedral solids such as  $\text{SiO}_2$ , phosphates, sulphates, etc., including mechanical as well as electronic properties, and glasses as well as crystals. We have also clarified the relation between the pseudopotential and bond orbital theories for simple covalent solids and seen why earlier attempts at understanding bonding in terms of pseudopotentials have failed. We hope to begin studies of transition-metal compounds next.

#### Publications:

1. W. A. Harrison, "Reply to Phillips" Comment on the Bond Orbital Model", Phys. Rev. Letters 34 1198 (1975).
2. W. A. Harrison, "Surface Reconstruction Semiconductors", Surface Science, 55, 1 (1976).
3. W. A. Harrison, Review of Metal-Insulator Transitions (N. F. Mott) and Electrical Conduction in Solid Materials (J. P. Suchet) Physics Today 29, 53 (February, 1976).
4. D. J. Chadi, R. M. White, and W. A. Harrison, "Theory of the Magnetic Susceptibility of Tetrahedral Semiconductors", Physical Review Letters Vol. 35, No. 20, 17 Nov. 1975.
5. R. Sokel and W. A. Harrison, "Long-Range Interactions in Semiconductors", Physical Review Letters Vol. 36, No. 1 5 January 1976.
6. Sokrates T. Pantelides and Walter A. Harrison, "Electronic Structure, Spectra, and Properties of 4:2-coordinated Materials. I. Crystalline and Amorphous  $\text{SiO}_2$  and  $\text{GeO}_2$ ", Physical Review B Vol. 13 No. 6 15 March 1976.
7. W. A. Harrison and R. Sokel, "Extension of the Gordon-Kim Overlap Interaction To Open Shell Systems", J. Chem. Phys. (in press).
8. W. A. Harrison and Sokrates T. Pantelides, "Oscillator Strengths in Tetrahedral Semiconductors", Phys. Review (in press).



## 29. DYNAMIC DARK-FIELD ELECTRON MICROSCOPY

G. B. Haydon, Senior Research Associate, Center for Materials Research

### Professional Associates:

M. K. Pyzyna  
C. R. Zercher

### Technical Objective:

Dynamic dark-field electron microscopy as described here provides capabilities not present with other methods. An annular ring of any selected diameter is used to illuminate the specimen. Diffraction rings selected by the objective aperture are integrated photographically to produce the dark-field image.

### Approach:

All methods of dark-field electron microscopy eliminate the incident illumination from the image and utilize only a selected portion of the scattered electrons and each has its limitations:

- (1) Movement of the objective aperture off of the optical axis introduces spherical aberration which increases as the 4th power of the distance from the axis.
- (2) Tilting the beam either mechanically or electrically allows only those electrons scattered in one direction to be imaged.
- (3) A hollow cone of illumination can be produced by a condenser aperture which must be carefully aligned and is subject to charging.
- (4) The central objective aperture stop method is also difficult to align and is subject to charging.

The second method can be accomplished electronically which allows a rapid change between dark-field and bright-field while the other methods require mechanical readjustment for changing modes.

## Research Report:

The dynamic dark-field method utilizes an electronic beam tilt, as in the second method, in conjunction with an electronic beam rotation to sweep out any selected cone of illumination. All of the diffraction rings, a segment of which are imaged with the sample beam tilt and thus swept through the objective aperture and summed by the phosphor persistence or photographically. The microscope image is then generated by the scattering in all directions which are admitted to the viewing system.

The system is equivalent to an annular objective aperture of variable size as determined by the beam tilt and whose width is determined by the objective aperture diameter.

Visually the technique is easy to use because the eye can adapt to the small dynamic changes when not critically adjusted. However, for photography the alignment requirements are more stringent but can be easily accomplished. A sin/cos generator has been introduced to drive the beam tilt coils of the standard Philips accessory on an EM200. The alignment trim pots on the Philips control panel are utilized to cause the beam to rotate around a fixed point in the specimen. The image must be near to true focus. The technique is easily used at all magnifications and once adjusted, changing from bright-field to dark-field and back is accomplished electronically.

The simple tilted beam dark-field method alone has a higher potential for contrast of favorably oriented single crystals because the diffuse scattering is reduced. The same field in dynamic dark-field, now in lower contrast, shows all crystals which are favorably oriented. The increased amount of diffuse scattering would also be present with the hollow cone illumination or central objective aperture stop methods.

Thus, all crystallites with a given orientation such that their diffraction fall in the ring swept by the objective aperture will appear in the image. By selecting successive rings for imaging different crystallites, multiple populations of orientation can be imaged from the same field. It should be possible to print each population in a different color such that a composite image

of a given field will show each orientation in a different color, greatly facilitating orientation distribution studies.

Reference Publication:

1. G. B. Haydon, R. A. Crane and C. R. Zercher, Proceedings, Thirty-third Annual Meeting, Electron Microscopy Society of America (1976), in press.

### 30. FRACTURE OF COMPACT BONE

W. C. Hayes, Assistant Professor, Applied Mechanics and Surgery (Orthopaedics)

#### Professional Associates:

D. A. Nagel  
D. J. Schurman

#### Graduate Students:

D. R. Carter  
S. T. Olson  
T. M. Wright

#### Agency Support:

NSF/MRL through CMR  
NIH AM18376-01  
Calif. Institute of Technology President's Fund

#### Technical Objectives:

To characterize fracture processes induced by dynamic and cyclic loads in specimens of bone and to correlate these processes with bone microstructure and density.

#### Research Report:

##### (1) Bone Fatigue Damage Accumulation

Graduate Student: D. R. Carter

This study examined the accumulation of damage in devitalized compact bone specimens as manifested by their loss of stiffness and strength during fatigue loading. Longitudinal bovine specimens were subjected to cyclic tensile and rotating cantilever tests. The results revealed a progressive loss of stiffness and strength comparable to stiffness and strength reductions observed in the fatigue of composite materials. The damage mechanisms as observed by scanning and reflected light microscopy consisted of: 1) cement line debonding in regions subjected to tensile fatigue damage; and 2) diffuse oblique cracking and longitudinal splitting in regions subjected to compressive

fatigue damage. The damage modes correspond to the morphology of clinically observed fatigue fractures.

(2) Bone Compressive Strength

Graduate Student: D. R. Carter

Cylindrical specimens of human subchondral trabecular bone were tested in uniaxial compression over 5 decades of strain rate ranging from 0.001 to 10 sec<sup>-1</sup>. Fifty specimens were tested with marrow in situ and 75 specimens with marrow removed. After testing, the specimen apparent density was determined. Marrow caused an increase in compressive strength only at the highest strain rate. The compressive strength of specimens tested without marrow was proportional to the square of the apparent density and to the strain rate raised to the 0.06 power. This relationship is applicable to the entire range of bone densities observed in the skeleton and thus provides clinical guidelines for assessing bone strength in patients with decreased skeletal mass.

(3) Tensile Properties of Compact Bone

Graduate Student: T. M. Wright

The objective of this investigation was to determine if a critical velocity exists for compact bone tested in tension over a wide range of strain rates. Highly significant positive correlations were observed between ultimate strength and strain rate and between ultimate strength and density. Modulus values showed similar correlations with test parameters. Multiple linear regressions were used to derive equations for ultimate strength and modulus as functions of strain rate, density and bone microstructure. A critical velocity where energy absorption capacity attained a maximum was not observed.

Reference Publications:

1. Carter, D. R. and Hayes, W. C., "Bone Fatigue Damage Accumulation", IRCS Abstracts, 3: 438, 1975.
2. Wright, T. M. and Hayes, W. C., "Longitudinal Fatigue Crack Propagation in Compact Bone", IRCS Abstracts, 3: 430, 1975.

3. Carter, D. R. and Hayes, W. C., "Fatigue Life of Compact Bone - I Effects of Stress Amplitude, Temperature, and Density", J. Biomechanics, 9: 27-34, 1976.
4. Carter, D. R., Hayes, W. C., and Schurman, D. J., "Fatigue Life of Compact Bone - II Effects of Microstructure and Density", J. Biomechanics, 9: 211-218, 1976.
5. Hayes, W. C. and Carter, D. R., "The Effect of Marrow on Energy Absorption of Trabecular Bone", Trans. Orthopaedic Research Society, 1: 10, 1976.
6. Hayes, W. C., Swenson, L. W., and Schurman, D. J., "Mechanics of Tibial Plateau Fractures", Trans. Orthopaedic Research Society, 1: 11, 1976.
7. Saha, S. and Hayes, W. C., "Tensile Impact Properties of Human Compact Bone", J. Biomechanics, 9: 243-251, 1976.
8. Hayes, W. C. and Carter, D. R., "Post-yield Behavior of Subchondral Trabecular Bone", J. Biomed. Mater. Res. Symp., 7, in press.
9. Wright, T. M. and Hayes, W. C., "The Fracture Mechanics of Fatigue Crack Propagation in Compact Bone", J. Biomed. Mater. Res. Symp., 7, in press.
10. Wright, T. M. and Hayes, W. C., "Tensile Testing of Bone Over a Wide Range of Strain Rates: Effects of Strain Rate, Microstructure and Density", Med. and Biol. Engineering, in press.
11. Carter, D. R. and Hayes, W. C., "Bone Compressive Strength: The Influence of Density and Strain Rate", Submitted to Science, March, 1976.

### 31. MECHANICAL BEHAVIOR OF COMPOSITES UNDER IMPACT

George Herrmann, Professor, Applied Mechanics

#### Graduate Students:

T. J. Delph

#### Agency Support:

AFOSR  
NSF/MRL through CMR

#### Technical Objectives:

As is generally recognized, two-phase composite materials, such as fiber-reinforced or layered solids, possess several features, which make them more attractive for certain technological applications than conventional macro-homogeneous materials. Thus the need arises to construct appropriate mathematical models to be used in describing analytically the mechanical behavior of such materials. It is the purpose of this program to develop suitable models and draw analogies to crystal lattice dynamics and the motions of electrons.

#### Approach:

In order to construct approximate theories, it is required to study in full detail the exact frequency spectrum of a layered composite which was never done before. The states of plane strain and anti-plane strain are studied in particular and the dispersion surfaces derived for these cases will be used as a guide in constructing approximate models.

#### Research Report:

- (1) On Continuum Modeling of the Dynamic Behavior of Layered Composites  
by G. Herrmann, R. K. Kaul, T. J. Delph

A hierarchy of new approximate continuum theories to model the dynamic behavior of layered composites, termed matched effective stiffness theories, is advanced. In each approximation the approximate frequency spectra are matched as closely as possible to the exact spectra,

and the range of validity of each approximation is ascertained. The procedure followed is conceptually not unlike that employed in deriving approximate plate theories. It requires an intimate knowledge of exact frequency spectra, together with the associated mode shapes. With the example of SH-waves propagating normal to the layering, it is shown that rather simple approximate field equations are capable of describing accurately the important filtering property of a composite, which none of the other approximate theories proposed by previous investigators were able to do. Similarities to certain phenomena in solid state physics are pointed out and, finally, an analogy to a system with one-degree-of freedom is drawn.

(2) On Coalescence of Frequencies and Conical Points in the Dispersion Spectra of Elastic Bodies by T.J. Delph, G. Herrmann, R.K. Kaul

In this paper we discuss a general procedure for determining the critical points in the dispersion spectrum at which there is a coalescence of frequencies, i.e. critical points which are roots of double multiplicity. We further show how the general behavior of the dispersion surface in the neighborhood of the critical points can be determined analytically. For the purpose of illustration, we consider

- (a) plane waves propagating in an infinite, isotropic plate, which corresponds to the case of a differential equation with constant coefficients, and
- (b) Floquet waves of the SH-type propagating in a layered medium, which corresponds to the case of a differential equation with periodic coefficients.

Reference Publications:

1. J. D. Colton and G. Herrmann, "Dynamic Fracture Process in Beams", Journal of Applied Mechanics, Vol. 42, No. 2, June 1975, pp. 435-439.
2. L. B. Freund and G. Herrmann, "Dynamic Fracture of a Beam or Plate in Plane Bending", Journal of Applied Mechanics, Vol. 43, No. 1,



March 1975, pp. 112-116.

3. R. K. Kaul and G. Herrmann, "A Note on Critical Reflections of Waves in an Isotropic Elastic Plate", International Journal of Solids and Structures, Vol. 12, No. 5, May 1976, pp. 353-357.

4. R. K. Kaul and G. Herrmann, "Free Torsional Vibrations of an Elastic Cylinder with Laminated Periodic Structure", International Journal of Solids and Structures, Vol. 12, No. 6, June 1976, pp. 449-466.

5. R. K. Kaul and G. Herrmann, "Torsional Vibrations of a Hollow Cylinder with Periodic Structures", to be published in the Proceedings of the Mechanical Engineering Conference, Pahlavi University, Shiraz, Iran (1975).

6. G. Herrmann, R. K. Kaul, T. J. Delph, "On Continuum Modeling of the Dynamic Behavior of Layered Composites", Archives of Mechanics, (Archiwum Mechaniki Stosowanej) No. 3, 1976.

## 32. STRUCTURAL STUDIES OF PROTEINS

Keith O. Hodgson, Assistant Professor, Chemistry

### Professional Associates:

A. Wlodawer  
J. Goodfellow

### Graduate Students:

S. P. Cramer  
T. K. Eccles  
F. Kutzler  
J. C. Phillips

### Agency Support:

NIH CA 16748  
PRF 2887-G3  
Research Corporation  
NSF through SSRP

### Technical Objective:

Investigation of the structures of biomacromolecules on a molecular level.

### Approach:

Two approaches are being used. We are applying conventional X-ray diffraction methods to investigate the crystal structures of three proteins, nerve growth factor, monellin and L-glutaminase-asparaginase. In addition, unconventional synchrotron radiation is being exploited as a source for X-ray diffraction studies as it offers high intensity and tunability. The second approach being used is that of extended X-ray absorption fine structure spectroscopy (EXAFS) to investigate the local geometry around the metal centers in metallo-enzymes. Information about the oxidation state and coordination site geometries in proteins such as nitrogenase, hemoglobin and hemocyanin is being obtained and is described herein.

Research Report:

(1) X-ray Diffraction Studies of Proteins Using Conventional and Synchrotron Radiation

Postdoctoral Fellows: A. Wlodawer  
J. Goodfellow

Graduate Students: J. Phillips

*Application of Anomalous Scattering to Phasing of X-ray Diffraction Data*

Seven  $hk0$  photographs of rubredoxin were obtained at SSRP during the last run. The photographs were each taken at a different wavelength, close to the iron K absorption edge. Three films were taken above the edge in energy, three were taken below, and one at the edge. Patterson maps were calculated for all seven films, using the differences between Friedel pairs as coefficients. The maps, from films taken above the edge, all had positive density at the iron site. This Fe peak grows progressively higher relative to background as the wavelength approaches the iron edge from the high energy side. Patterson maps calculated for the film at the edge and for the film just below the edge had peaks at the iron site but well below background. Maps calculated from the other two films further below the edge give no indication of the iron site.

Patterson coefficients have also been calculated based only on changes in the real part of the anomalous scattering. This was done by combining data from a film recorded just below the edge with that from a film far below the edge, treating the data as the native and isomorphous derivative respectively. The resulting Patterson map had signal-to-noise for the iron site as good as the best map based on Friedel pair differences. A further technique was used in which Friedel pair differences from the best film above the edge were combined with the 'real part' differences. This was done using the method for combining isomorphous and anomalous differences proposed by Kartha and Parthasarathy and Matthews. This method gives 'exact' Patterson coefficients. The resulting map had the best signal-to-noise for the iron site of any calculated. (The S/N ratio was improved from 1.2 to 1.5.)

These results, while preliminary, suggest that the ability to

vary the monochromatic wavelength when using synchrotron radiation will have important implications on our ability to determine phases. We are currently applying the three-wavelength method to attempt to phase the  $hko$  reflections based on the changes in anomalous scattering.

We plan to apply this method in practice to study the structure of a small polypeptide ion carrier, gramicidin A. Crystals of the native material have been obtained and a data set collected. We are doing experiments in collaboration with L. Stryer to replace the N-terminal amino acid with iodinated phenylalanine. The substitution of p-iodo-L-phenylalanine has recently been shown to have little effect on physiological activity yet the iodine atom provides a convenient 'heavy atom marker' which can be used to phase the structure through anomalous scattering techniques. The actual data collection experiments are planned for the fall run at SSRP. Knowledge of the single crystal structure of this bimolecule will provide important verification of the "dimer-pore" concept of how it transports ions across bilayers.

## (2) Extended X-ray Absorption Fine Structure Spectroscopy

Graduate Students:     S. P. Cramer  
                             T. K. Eccles  
                             F. Kutzler

X-ray absorption spectra are characterized by several sharp edges of rapidly increasing absorption coefficient  $\mu$ . Closer examination of the high energy side of the edges reveals periodic damped oscillations in  $\mu$ ; this Extended X-ray Absorption Fine Structure has been called EXAFS. Using the Stanford electron storage ring SPEAR as an X-ray source, we are developing EXAFS Spectroscopy as a tool for the study of metalloproteins. Recent developments have been in studies of the local structure and oxidation level of the Mo atoms in nitrogenase and in the investigation of the Cu atom environment in the oxygen transport protein hemocyanin. In data analysis, a more quantitative understanding of the amplitude function for backscattering is providing the basis for using the envelope modulation of the extended fine structure to identify the type of ligating atoms surrounding the absorbing metal atom.

### *Backscattering Amplitude Functions*

The analysis of fine structure data from simple Mo compounds containing a single shell of either oxygen or sulfur atoms has shown that the amplitude behavior in the EXAFS spectrum is characteristic of the type of backscattering atom. The amplitude behavior for backscattering from the O atoms in  $\text{MoO}_4^{2-}$  is described by a simple exponential which falls off with increasing  $k$ . In contrast, the amplitude behavior for S backscattering in  $\text{MoS}_4^{2-}$  can be seen to peak and then begin to fall off. From the fit of our functional form to the data, we have quantitative forms for the amplitude function for S and O atomic types. A comparison of the peak of the amplitude in the S compound (taken from a plot of the data versus  $k$ , not  $k^2$ ) shows that the maximum occurs at  $k = 4.5 \text{ \AA}^{-1}$ . Recent electron atom scattering calculations done for us by M. Blaha show that the calculated scattering function peaks in the same place.

These results provide unambiguous evidence that the amplitude behavior can be used to obtain information on the type of atom which is backscattering. Further studies are in progress to determine how successfully this method can be used to distinguish between atoms with lower atomic numbers than O and S. The results are also being applied to interpret the protein data as described below.

### *EXAFS Studies on the Mo Atoms in Nitrogenase*

In an earlier communication, we reported that the oxidation level of the Mo atoms in the oxidized form of the lyophilized "Mo-Fe" component of nitrogenase was probably  $\text{Mo(V)}^{2+}$ . The uncertainty occurred only because the nature of the ligation of the Mo atoms was unknown at the time (the coordination charge is affected by the type and number of ligands).

Recently we have redetermined the edge position for the oxidized form as well as studied a reduced form of the "Mo-Fe" component of nitrogenase. The shift in edge position is shown to be correlated with a 2 electron change in oxidation level. If one assumes the presence of several sulfur ligands as indicated below, then this leads to the

conclusion that the two levels are Mo(III) and Mo(V). Data will be taken this month on solutions of the frozen protein in several different oxidation levels. These results will be correlated with esr spectra of the same solution and should definitively identify the role of the Mo atoms in these oxidation-reduction processes.

Analysis of the extended fine structure data from the Mo atoms in nitrogenase has led to the first conclusions about the environment of the Mo. A striking feature of the normalized fine structure data from the Mo atoms is the presence of a peaking in the amplitude function (similar to that seen with  $\text{MoS}_4^{2-}$  as opposed to  $\text{MoO}_4^{2-}$ ). Radial transforms of the  $\text{MoO}_4^{2-}$  data and the  $\text{MoS}_4^{2-}$  data have the "phase-shifted" Mo-O and Mo-S distances at 1.37 and 1.75 Å respectively (the actual distances are 1.76 and 2.16 Å). Most dominant in the nitrogenase transform is the peak at 1.86 Å which is indicative of the presence of a reasonably large number (greater than 2) of S (or similar Z) atoms directly ligating the Mo. The higher R peak (2.26 Å) is at too large a distance to be a coordinated S. It is likely due to the presence of another higher Z element (Fe or Mo) at a larger distance.

These results are being quantified by numerical analysis methods which we have shown to be more accurate and reliable than Fourier transform methods.<sup>3</sup> The procedure which is being followed is to isolate the peak of interest in R space (for example, the S peak in the nitrogenase data), window out the other peaks with a gaussian centered over the desired peak and retransform to  $k$  space. Numerical analysis methods are then used to analyze the phase and amplitude function of the "single shell" as described previously.<sup>3</sup>

These results have provided the first available evidence about the nature of the ligands surrounding the Mo atoms in nitrogenase. Further studies of the protein in solution will be used to look for the presence of Mo substrate interactions in the functioning enzymatic system using difference analysis techniques that have already been developed. These solution studies are being carried out in a collaborative effort with Mel Klein and his group at Berkeley.

Reference Publications:

1. J. C. Phillips, A. Wlodawer, M. Yevitz, and K. O. Hodgson, "Applications of Synchrotron Radiation to Protein Crystallography: Preliminary Results," *Proc. Nat. Acad. Sci. U.S.A.*, 73, 128 (1976).
2. S. P. Cramer, T. K. Eccles, F. Kutzler, K. O. Hodgson, and L. E. Mortenson, "Mo X-ray Absorption Edge Spectra - The Chemical State of Mo in Nitrogenase," *J. Amer. Chem. Soc.*, 98, 1287 (1976).
3. S. P. Cramer, T. K. Eccles, F. Kutzler, K. O. Hodgson, and S. Doniach, "Applications of X-ray Photoabsorption Spectroscopy to the Determination of Local Structure in Organometallic Compounds," *J. Amer. Chem. Soc.*, 98, 0000 (1976). (Also published as Stanford Synchrotron Radiation Report No. 75/10.)

33. PHYSICAL STUDIES OF MOLECULES OF BIOLOGICAL INTEREST

B. S. Hudson, Assistant Professor, Chemistry

Professional Associates:

A. Lu  
A. Waleh

Graduate Students:

J. R. Andrews	R. E. Jacobs
J. Bjarnason	H. A. Karp
S. P. Cramer	N. E. Schlotter
J. H. Dawson	L. A. Sklar
J. J. Diamond	S. G. Stanton
W. M. Hetherington III	F. K. Wolber

Agency Support:

Alfred P. Sloan Foundation	NIH CA 15461
Camille and Henry Dreyfus Foundation	NIH GM 21149
American Cancer Society	NIH EY 01518
American Chemical Society	

Technical Objectives:

The development of new methods for the study of large organic molecules and biomolecules especially using electronic and vibrational spectroscopy. Current interest centers on fluorescence, Raman and inelastic neutron scattering techniques and nonlinear Raman spectroscopy. Theoretical procedures are used in the design and analysis of experiments.

Approach:

Electronic energy levels of large conjugated organic molecules are studied by investigation of mixed crystal (solid solution) samples near the absolute zero of temperature. The vibrational motions of large molecules are studied by Raman and inelastic neutron scattering techniques coupled to consistent force field conformational and normal mode calculations. Buoyant density ultracentrifugation methods are



used in conjunction with room temperature fluorescence in the study of closed circular DNA. Resonance Raman methods are used to study both electronic and vibrational levels in conjugated molecules. Linear conjugated polyenes are used as fluorescence and Raman probes of membrane structure. An exciting new nonlinear Raman technique known as coherent anti-Stokes Raman scattering (CARS) is being developed.

Research Report:

(1) The Electronic Spectroscopy of Linear Polyenes

(see references 1-3)

Graduate Students: J. J. Diamond  
W. M. Hetherington III

Linear polyenes are conjugated chains of alternating double and single carbon-carbon bonds. Their electronic spectroscopy is of interest from the biological point of view because the visual pigments contain a linear polyene as the photoactive unit. These molecules are also of interest from a theoretical point of view because they are apparently inadequately described by most simple molecular orbital theories. It has recently been shown that the lowest energy excited singlet state of all linear polyenes consists of a mixture of singly and doubly excited configurations in the molecular orbital picture or to an exciton state derived from two ethylene triplet excitations (see reference 1). Resonance Raman experiments have confirmed the assignment of the vibrational intervals observed in the high resolution mixed crystal spectra of the polyene diphenyloctatetraene. A method has been found for the synthesis of linear polyenes which are part of a long saturated fatty acid chain. Mixed crystals of these polyenes,  $\beta$ -carotene, stilbene and other molecules of interest have been prepared. The implications of this revised state ordering for the photochemistry of polyenes is also being investigated. Two-photon spectral studies of linear polyenes are in progress. Photoelectron and electron impact spectroscopy have been applied to polyene spectroscopy (references 2 and 3). Recent progress in the synthesis of very long chain polymeric polyenes (polydiacetylenes) has opened up a

new interest in polyenes as materials.

(2) Improved Dye-Buoyant Density Procedure for the Isolation of Closed Circular DNA

Graduate Student: J. Dawson

Many organisms (including man) contain DNA in which both of the phosphodiester backbone chains are in the form of covalent circles. These molecules are of great medical interest because of their presence in animal tumor viruses and the occurrence of unusual closed circular forms in leukemia patients. A very efficient procedure for the preparation of closed circular DNA involves the interaction of the dye ethidium bromide with DNA in a buoyant density gradient. The buoyant density mixture consists of water, ethidium bromide, cesium chloride and the DNA of interest. At equilibrium, there is a separation between closed circular DNA and linear DNA or circular molecules which have suffered at least one backbone strand scission. The DNA bands are easily detected because of the enhanced fluorescence of the ethidium cation when it is bound to DNA. We have recently significantly improved the resolution of this technique by modification of the ethidium nucleus. A modification of this procedure has also been devised such that the fluorescence detection sensitivity of the DNA bands is so large that it is competitive with radioactive tracer methods.

(3) The Electronic Spectroscopy of Ethidium Bromide

Postdoctoral Research Associate: A. Waleh

Graduate Student: R. Jacobs  
(see references 4 and 5)

Ethidium bromide is a complex heterocyclic molecule used in the dye-buoyant density procedure described above. Ethidium has a very poor fluorescence quantum yield in water. When the molecule binds to DNA, its fluorescence is enhanced by about 25 fold. This fluorescence enhancement is the basis for a very useful detection method for DNA species. For this reason, and because of its intrinsic interest, we

would like to understand the mechanism for the fluorescence enhancement of ethidium. The problem is made even more interesting by the fact that other molecules with structures similar to ethidium which bind to DNA by the same mechanism show a decrease in fluorescence on binding. The fluorescence enhancement for ethidium is due to a change in the radiationless decay rate for the lowest energy excited singlet state. We have obtained preliminary evidence that the decay of this state occurs primarily by intersystem crossing to a triplet level which is nearly degenerate with the lowest singlet. The singlet level shifts below this triplet on binding to DNA and thus the decay channel is closed. Magnetic circular dichroism and low temperature absorption studies of ethidium have greatly increased our knowledge of the excited singlet levels. This knowledge will be used in conjunction with phosphorescence and triplet-triplet absorption experiments to determine the energies of the triplet levels. Recent molecular orbital calculations have confirmed the existence of an ethidium triplet level nearly degenerate with the lowest singlet level.

(4) Studies of Membrane Structure and Dynamics by Raman and Fluorescence Methods

Postdoctoral Research Associate: A. Lu

Graduate Students: L. A. Sklar  
(see references 6-8) J. R. Andrews

The structure and properties of phospholipid bilayers is a subject of great current interest because of the relevance of these studies to an understanding of the function of biological membranes. We are studying these structures by a combination of Raman, resonance Raman and fluorescence label techniques. The Raman studies are based on the fact that the normal modes of the hydrocarbon side chains of phospholipids are sensitive to the conformation of the chain. An analysis of the observed spectra using the normal coordinate analysis methods described below will yield information on the conformational changes of the phospholipids. Measurements of the degree of polarization of the Raman lines should yield information on the spatial distribution of

the various conformational species. Fatty acids containing conjugated polyene chains have been synthesized and incorporated into phospholipid bilayers. These probe molecules can be observed by resonance enhanced Raman spectroscopy and fluorescence. They will accept energy from excited aromatic amino acids so that energy transfer experiments are possible. The fluorescence intensity of the polyene probes is very sensitive to the phase transition behavior of model membrane systems and we expect that it will also be sensitive to the transmembrane electric field. These polyene probes are biologically incorporated into membranes by living organisms and can be detected with very high sensitivity ( $10^{-8}$  molar). Resonance enhanced depolarized Rayleigh scattering has been demonstrated (ref. 8) and will be a useful technique in studying the dynamics of these probe molecules in membranes.

(5) Consistent Force Field Calculations and Inelastic Neutron Scattering Spectroscopy (see reference 9)

Graduate Student: H. A. Karp

Inelastic neutron scattering spectroscopy can be used as a technique for molecular vibration spectroscopy similar to Raman scattering. Neutron scattering differs from optical methods in that many low frequency normal modes which are very weak or absent in IR and Raman spectra are strong in the neutron scattering spectra. Neutron scattering is interesting from the theoretical point of view because the intensities of inelastic events can be calculated from an assumed knowledge of the nuclear vibrational motion. This is in contrast to the calculation of IR and Raman intensities where a knowledge of dipole and polarizability changes must be available. The information needed for a neutron scattering calculation consists of the vibrational normal mode eigenvalues and eigenvectors which can be obtained from a reliable normal mode calculation. We have used the consistent force field potential of Lifson and Warshel to calculate neutron scattering spectra of saturated hydrocarbons. The parameters for the force field were taken from Lifson and Warshel who had adapted them to fit

conformational, vibrational and thermodynamic data. The agreement between calculated and observed inelastic neutron scattering spectra was very good. Experimental work is under way involving neutron scattering spectra of molecular crystals and model membrane systems.

(6) Coherent Anti-Stokes Raman Scattering (see references 10 and 11)

Graduate Students: J. Bjarnason  
S. P. Cramer  
W. Hetherington III

Coherent anti-Stokes Raman scattering (CARS) is an exciting new technique for obtaining Raman spectra with very high signal levels and high signal to noise ratios. The technique involves a nonlinear mixing process which results in a very high conversion of incident power to signal when two high peak power pulses with different frequencies are crossed in a sample. A high signal to noise ratio occurs because the signal is produced as a coherent beam and because no monochromator is needed (the spectrum is scanned by varying the frequency difference between the two incident beams). This technique can be used to strongly discriminate against fluorescence because of the low spatial divergence of the signal beam and because of the anti-Stokes frequency. This technique is ideally suited to studies of dilute biological systems containing chromophores by resonance enhanced CARS scattering. One of the many advantages of CARS is that low average power levels are used which minimizes sample damage. A particularly exciting application of CARS involves the detection of vibrational optical activity via circular intensity differential Raman scattering. Resonance enhancement of CARS scattering has been demonstrated and the conventional theory of the CARS cross section has been extended to include the complex nature of the third order susceptibility near an electronic resonance.

Reference Publications:

1. Bruce S. Hudson and Bryan E. Kohler, "Linear Polyene Electronic Structure and Spectroscopy," Ann. Rev. Phys. Chem. 25, 437 (1974).

2. Bruce S. Hudson, James Diamond and J. N. A. Ridyard, "Polyene Spectroscopy: Photoelectron Spectra of the Diphenylpolyenes," J. Am. Chem. Soc. 98, 1126 (1976).
3. Douglass E. Post, William Hetherington III and Bruce S. Hudson, "100 eV Electron Impact Spectra of Hexatriene," Chem. Phys. Lett. 35, 259 (1975).
4. Bruce S. Hudson and Russell E. Jacobs, "The Ultraviolet Transitions of the Ethidium Cation," Biopolymers 14, 1309 (1975).
5. Ahmad Waleh, Bruce S. Hudson and Gilda Loew, "Excited Electronic States of the Ethidium Cation," Biopolymers, in press.
6. Larry A. Sklar, Bruce S. Hudson and Robert D. Simoni, "Conjugated Polyene Fatty Acids as Membrane Probes: Preliminary Characterization," Proc. Nat. Acad. Sci. USA 72, 1649 (1975).
7. Larry A. Sklar, Bruce S. Hudson and Robert D. Simoni, "Conjugated Polyene Fatty Acids as Fluorescent Membrane Probes: Model System Studies," J. Supramolecular Structure 4, 449 (1976).
8. David R. Bauer, Bruce S. Hudson and Robert Pecora, "Resonance Enhanced Depolarized Rayleigh Scattering from Diphenylpolyenes," J. Chem. Phys. 63, 588 (1975).
9. Bruce S. Hudson, Hilary Karp and Sow-Hsin Chen, "Pseudo-rotational Motion of Methylcyclopentane Observed by Neutron Inelastic Scattering," J. Chem. Phys. 62, 4564 (1975).
10. Richard F. Begley, A. B. Harvey, Robert L. Byer and Bruce S. Hudson, "Raman Spectroscopy with Intense, Coherent, Anti-Stokes Beams," J. Chem. Phys. 61, 2466 (1974).
11. Ilan Chabay, Gary Klauminzer and Bruce S. Hudson, "Coherent Anti-Stokes Raman Spectroscopy (CARS): Improved Experimental Design and Observation of New Higher Order Processes," Appl. Phys. Lett. 28, 27 (1976).

#### 34. SOLID STATE ELECTROCHEMISTRY

R. A. Huggins, Professor, Materials Science and Engineering

##### Professional Associates:

B. A. Boukamp  
A. G. Elliot  
D. Elwell  
N. Endow  
R. S. Feigelson  
I. D. Raistrick  
W. Weppner

##### Graduate Students:

O. B. Ajayi\*  
U. Cohen  
C. V. H. Fuchs\*\*  
N. A. Godshall  
T. M. Gur\*  
E. E. Hellstrom  
C. Ho  
Y. W. Hu  
J. E. Leiss  
B. E. Liebert

\*Received PhD during report period.  
\*\*Received MS during report period.

##### Agency Support:

ONR N00014-75-C-1056  
ARPA through CMR

##### Technical Objectives:

(1) Development of new materials for use in solid state electrochemical systems. This involves design, synthesis and characterization of new inorganic materials as well as evaluation of their structure, thermodynamic and transport properties. Potential areas of application involve high performance battery and fuel cell systems, catalysts, selective ion sensors and electrochromic display devices.

(2) Achievement of understanding concerning the important phenomena involved in the rapid transport of atoms in solid electrolytes and mixed conductors and their structural basis.

(3) Investigation of new techniques for materials synthesis, including electrocrystallization of metals, alloys, and semiconducting

and metal-metalloid compounds, and the controlled decomposition and reaction of infiltrated polymeric precursors to make oxides and metals.

#### Research Report:

##### (1) Mass and Charge Transport in Fast Ion Conductors

Theoretical models have been developed and experimental measurements made of the defect structure, and ionic and electronic conductivity in several groups of solids with highly mobile ionic species. Particular attention has been devoted to materials with crystal structures containing crystallographic tunnels and sparsely populated sites. These have included beta alumina, alkali metal ferrocyanides, titanates, germanates, silicates, aluminosilicates, fluorides and related materials. Current work involves measurements on several groups of promising lithium ion conductors.

Experimental methods being utilized include nuclear magnetic resonance and ionic conductivity measurements, as well as several techniques for the evaluation of time-dependent transport in solid state electrochemical systems.

##### (2) Use of Solid State Electrochemical Techniques to Influence Catalysis

Elevated temperature solid state electrochemical cell techniques are being developed and used to characterize and control the defect structure and properties of metals and mixed conductors to study and modify their catalytic properties. Primary effort has been directed at studies of the catalytic decomposition of nitric oxide, a common constituent of exhaust gases, on  $\text{ZrO}_2$  and  $\text{ZrO}_2$ -Pt systems. It has been found that the reaction rate on supported platinum can be greatly enhanced, and under proper conditions can be even more rapid upon bare reduced  $\text{ZrO}_2$ .

##### (3) Synthesis and Structure of Materials with Intercalated Layer Structures

Several techniques have been used to synthesize and study groups of materials with intercalated layer structures. Recent work involved graphite compounds, some of which appear to be particularly interesting as battery components, and as possible catalysts.



(4) Exploration of a New Method for the Synthesis of Oxides

A new method, involving the controlled decomposition of salt-infiltrated polymeric precursors, is being explored for the synthesis of oxides and other compounds. Current work is aimed at the preparation of beta alumina, an important solid electrolyte.

(5) Novel Solid State Battery and Fuel Cell Systems

Several new concepts for the development of high performance batteries and fuel cells based upon the use of solid and liquid electrolytes are being explored. Particularly interesting are systems with high values of energy density utilizing mixed-conducting solids as electrode components.

(6) Development of Electrochemical Techniques for Crystal Growth

Both theoretical and experimental work are underway on the use of electrochemical techniques for the growth of both single crystals and polycrystals. Of particular interest at the present time is electrocrystallization of intermetallic and metal-metalloid compounds from molten salt systems. Materials being studied include niobium superconducting compounds, sulfides, phosphides, hexaborides, and materials with the tungsten bronze and related structures.

Reference Publications:

1. D. Elwell, I. V. Zubeck, R. S. Feigelson and R. A. Huggins, "Surface Structure and Electrolytic Growth Stability of  $\text{LaB}_6$  Crystals", J. Crystal Growth 29, 65 (1975).
2. S. Pancharatnam, R. A. Huggins and D. E. Mason, "Catalytic Decomposition of Nitric Oxide on Zirconia by Electrolytic Removal of Oxygen", J. Electrochem. Soc. 122, 869 (1975).
3. J. Schoonman, L. B. Ebert, C.-H. Hsieh and R. A. Huggins, "Ionic Motion in  $\beta\text{-PbF}_2$ ", J. Appl. Phys. 46, 2873 (1975).
4. J. Schoonman and R. A. Huggins, "Composition Dependence of Ionic Conductivity", J. Phys. Chem. Solids 36, 815 (1975).
5. R. A. Huggins, "Alkali Ion Transport in Materials of the Beta Alumina Family", in Mass Transport Phenomena in Ceramics, Eds. A. R. Cooper and A. H. Heuer, Plenum Press (1975), p. 155.

6. A. G. Elliot and R. A. Huggins, "Phases in the System  $\text{NaAlO}_2\text{-Al}_2\text{O}_3$ ", J. Amer. Ceramic Soc. 58 (11), 497 (1975).
7. O. B. Ajayi, L. E. Nagel, I. D. Raistrick and R. A. Huggins, "Calculation of Motional Activation Energies for Interstitial Ions in the Rutile Structure Using a Minimum Energy Path Model", J. Phys. Chem. Solids 37, 167 (1976).
8. R. A. Huggins, "Basic Research in Materials", SCIENCE 191, 647 (1976).
9. U. Cohen and R. A. Huggins, "Silicon Epitaxial Growth by Electrodeposition from Molten Fluorides", J. Electrochem. Soc. 123, 381 (1976).
10. J. Schoonman and R. A. Huggins, "Electrical Properties of Undoped and Doped Potassium Tetrafluoroaluminate:  $\text{KAlF}_4$ ", J. Solid State Chem. 16, 413 (1976).
11. I. D. Raistrick and R. A. Huggins, "Considerations in the Use of Electrical Measurement Techniques to Evaluate Potential New Electrolytes and Mixed Conductors", in Proceedings, Symposium and Workshop on Advanced Battery Research and Design, Argonne National Laboratory (1976) p. B-277.
12. B. E. Liebert and R. A. Huggins, "Ionic Conductivity of  $\text{Li}_4\text{GeO}_4$ ,  $\text{Li}_2\text{GeO}_3$  and  $\text{Li}_2\text{Ge}_7\text{O}_{15}$ ", Mat. Res. Bull. 11, 533 (1976).
13. D. Elwell, R. C. DeMattei, I. V. Zubeck, R. S. Feigelson and R. A. Huggins, "D C Resistances in Electrolytic Crystallization from Molten Salts", J. Crystal Growth 33, 232 (1976).
14. L. B. Ebert, R. A. Huggins and J. I. Brauman, "Reaction of Antimony Pentafluoride with Poly(Carbon Monofluoride)", Mat. Res. Bull. 11, 615 (1976).

### 35. ACOUSTIC INTERACTIONS WITH SOLIDS

G. S. Kino, Professor, Electrical Engineering

#### Professional Associates:

P. Khuri-Yakub  
T. Waugh

#### Graduate Students:

P. G. Borden	R. Joly*
C. S. DeSilets	H. C. Tuan
J. D. Fraser	J. Souquet

#### Agency Support:

\*Received PhD during Report Period.

NSF ENG75-18681  
AF F-30602-74-C-0038  
AMROC RI 74-20773  
N00014-76-C-0129  
N00123-75-C-1355  
N00014-75-C-0632  
EPRI RP 609-1

NSF/MRL through CMR - Thrust Program on Use of Acoustic Techniques  
for the Characterization of Materials

#### I. Acoustic Surface Wave Convolvers

##### Technical Objective:

To construct acoustic surface wave convolvers which can store electrical signals, correlate or convolve two electrical signals with each other, and take various type of transforms of signals. In addition, we are interested in using such convolvers for infrared and optical imaging and to take spatial transforms of such images.

##### Approach:

The basic convolver makes use of the interaction between the electrical fields associated with an acoustic surface wave in a piezoelectric material and a neighboring slab of silicon. Two types of convolvers are being investigated: 1) the surface wave is propagated on a piezoelectrical material,  $\text{LiNbO}_3$ , and the silicon is separated mechanically from the  $\text{LiNbO}_3$  by an airgap of the order of  $1000 \text{ \AA}$ ; 2) a piezoelectric material,  $\text{ZnO}$ , is rf sputter deposited on Si.

## Research Report:

The materials technology for convolvers has been radically improved during the last year. We have made a mechanically stable and uniform airgap convolver configuration in which rails 4  $\mu\text{m}$  wide are etched in  $\text{LiNbO}_3$  by sputtering techniques, and used to separate the Si and  $\text{LiNbO}_3$ . A further advance is to use either Schottky barriers or an array of p-n junctions laid down in the Si. Interaction between the acoustic surface waves and the Si then takes place in the depletion layers of these diodes, rather than at the surface, thus removing many of the problems associated with surface effects. By etching triangular grooves between the junctions, it is possible to separate out the individual elements, and, thus, cause there to be essentially zero interaction between the individual diodes.

The same kind of approach has been used with ZnO on Si devices. The buried diode techniques tend to eliminate the problems associated with traps in ZnO, as well as surface effects. Thus, the reliability of the ZnO on Si devices has been radically improved.

With these devices, we have been able to store electrical signals for tens of milliseconds and we have been able to take the correlation between a stored input signal and a later signal inserted into the device, with time bandwidth products of the order of 100. The devices have also been used for optical imaging, and, in particular, for carrying out spatial Fourier transforms in real time of optical images. The concepts involved open up new techniques of signal processing in real time which are extremely difficult to accomplish by other methods.

## II. Nondestructive Testing

### Technical Objective:

To use acoustic techniques to determine the location and size of flaws in materials, and determine more subtle properties of materials such as residual stress.

### Approach:

Acoustical imaging techniques in which an array of piezoelectric transducers is employed have been shown to produce good images of

flaws in metal samples. Related techniques have been applied to measure stress profiles in metal and to measure extremely small flaws in ceramics of the order of 50  $\mu\text{m}$  diameter.

#### Research Report:

We have continued work on the electronically scanned and focused acoustic imaging system previously described. This system, which operates at approximately 2 MHz, employs a piezoelectric transducer array of 32 elements, which can be used as a transmitter and receiver. The system can be electronically scanned and focused in the reflection mode to produce a TV raster image in real time of a plane normal to the face of the array. We are able to scan a field 6 cm  $\times$  26 cm with 10 lines/frame and 16 frames/second. The resolution of this system is approximately 2mm in each direction. This same system can also be operated in a transmission mode, i.e., with a transmitter array facing a received array, with a similar resolution.

We have recently set the system up for reflection mode imaging with shear waves in aluminum and have obtained good images of an array of 3 mm diameter holes drilled in the samples at a distance of 15 cm from the array.

Similar results have been obtained with electronically focused and scanned Rayleigh waves propagated along the surface of a metal sample.

Recently, we have operated a mechanically scanned lens focused single transducer in a reflection mode. By using an rf reference, we have been able to measure small changes in acoustic velocity in metal samples. Such small changes in velocity occur when the material is stressed. Thus, by this means, we have been able to map out the stressed regions in the neighborhood of a fatigue crack in steel.

The same techniques are now being scaled to operate at 200 MHz. We are using 2 ns pulses injected into a ZnO on sapphire transducer. By this means, we can detect flaws in ceramic materials suitable for use in turbine blades, such as  $\text{Si}_3\text{N}_4$ ,  $\text{SiC}$ . The resolution is of the order of 50  $\mu\text{m}$ .

#### Reference Publications:

1. H. Gautier, "Acoustic Wave Semiconductor Convolver Applied to Electrical and Optical Signal Processing," M.L. Report No. 2448, Microwave Laboratory, Stanford University, 1975.\*
2. B. T. Khuri-Yakub, "The Application of Zinc Oxide on Silicon to Surface Acoustic Wave Devices," M.L. Report No. 2509, Microwave Laboratory, Stanford University, 1975.\*
3. R. Joly, "Design of a Convolver for Optical Imaging," M.L. Report No. 2560, Edward L. Ginzton Laboratory, Stanford University, 1976.\*
4. J. Fraser, J. Havlice, G. Kino, W. Leung, H. Shaw, K. Toda, T. Waugh, D. Winslow, and L. Zitelli, "An Electronically Focused Two-Dimensional Acoustic Imaging System," *Acoustical Holography*, 6, pp. 275-304, Plenum Press, 1975.
5. G. S. Kino and A. G. Evans, "Non-Destructive Evaluation of Ceramics," Report for ARPA/MRC Council, July 1975. G.L. Internal Memo No. 2571, 1976. Ginzton Laboratory, Stanford University.
6. B. T. Khuri-Yakub, G. S. Kino, and P. Galle, "Studies of the Optimum Conditions for Growth of RF Sputter ZnO Films," *J. Appl. Phys.*, 46, 3266-3272, August, 1975.
7. G. S. Kino, C. DeSilets, J. Fraser, and T. Waugh, "New Acoustic Imaging Systems for Non-Destructive Testing," *IEEE Ultrasonics Symposium Proceedings*, September 1975.
8. C. S. DeSilets, J. Fraser, and G. S. Kino, "Transducer Arrays Suitable for Acoustic Imaging," *IEEE Ultrasonics Symposium Proceedings*, September, 1975.
9. H. Gautier and G. S. Kino, "A Detailed Theory of the Acoustic Wave Semiconductor Convolver," M.L. Report No. 2479, Microwave Laboratory, Stanford University, 1975. To be published in *IEEE Transactions on Sonics and Ultrasonics*.
10. G. S. Kino, "Applications of Electronically Scanned Acoustic Imaging Techniques to NDE," *Proc. ARPA/AFML Review of Quantitative NDE*, pp. 303-319, January 1976.
11. G. S. Kino, "Acoustoelectric Interactions in Acoustic Surface Wave Devices," M. L. Report No. 2518, invited paper, *Proc. IEEE, Special Issue on Acoustic Wave Technology*, May 1976.
12. G. S. Kino, "A Review of Some Possible Applications of Acoustic Convolver Technology," invited paper, *Proc. Reunion Internationale organisee par la DRME*, pp. 113-184, April, 1976

13. B. T. Khuri-Yakub and G. S. Kino, "A Detailed Theory of the Monolithic Zinc Oxide on Silicon Convolver," G.L. Report No. 2541, to be published in IEEE Trans. on Sonics and Ultrasonics, 1976.
14. B. T. Khuri-Yakub and G. S. Kino, "A Monolithic Waveguide Zinc Oxide on Silicon Convolver," G. L. Report No. 2540, Ginzton Laboratory, Stanford University, 1976, to be published in Electronics Letters.

~ \*Thesis

36. ANALYSIS OF METAL-FORMING, IMPACT, WAVE PROPAGATION IN HETEROGENEOUS MEDIA AND FORMULATION OF CONSTITUTIVE RELATIONS

E. H. Lee, Professor, Applied Mechanics

Professional Associates:

R. L. Mallett

Graduate Students:

K. A. Derbalian

G. A. Nystrom\*

R. W. Young\*

T. B. Wertheimer\*\*

\* Received PhD during report period.

\*\* Received MS during report period.

Agency Support:

ONR N00014-75-C-0698

ONR-ARPA N0014-75-C-0923

NSF NSF-ENG-75-17376

NSF/MRL through CMR - Thrust Program on the Application of the Finite Element Method to the Study of Deformation and Fracture of Metals

Technical Objectives:

A complete stress-analysis of a metal-forming process is necessary in order to assess the onset of metal-forming defects such as the initiation of internal or surface cracks or the generation of residual stresses. In order to evaluate stresses throughout the material it is necessary to carry out an elastic-plastic analysis since rigid-plastic theory can only predict stresses in the regions exhibiting significant current plastic flow. Our objective is to develop a program to evaluate complete stress-distributions and to apply it initially to the extrusion process. Such solutions have not previously been obtained for general two and three dimensional problems encompassing the technologically important steady state processes, although they are essential for the rational assessment of limits on process variables which will ensure a satisfactory metal-forming procedure.



#### Approach:

Elastic-plastic theory relates rate of stress and rate of strain with current stress and deformation history influencing the coefficients. When plastic flow sets in, the tangent modulus is of the order of the stress for many metals, and this circumstance, combined with the rate relations, introduces the need to include convected translational and rotational terms and geometrical non-linearities into the analysis. These can be conveniently incorporated by utilizing a referential or Lagrange type formulation. However, the incremental or fluid-like nature of plasticity commends a spacial or Euler type formulation, and this can be achieved, in combination with the advantage of a fixed reference frame, by using a sequentially updated reference state for each time step in the calculation. This permits convenient inclusion of nonlinear terms associated with the development of finite deformation. A finite element program incorporating the effects already mentioned has been developed to analyze extrusion problems.

#### Research Report:

##### (1) Finite Element Analysis

Graduate Students: K. A. Derbalian

T. B. Wertheimer

In order to satisfy the boundary conditions of the metal sliding over the surface of a curved die, the variational principle in terms of velocities previously presented by Hill had to be generalized somewhat. Also, in order for the calculation to encompass steady-state extrusion, special care in the selection of finite element geometry had to be exercised to prevent the constraint of virtually incompressible deformation from invalidating the power of the variational principle to generate the solution following significant plastic flow.

The elastic-plastic solution of a sheet extrusion problem in plane strain has been evaluated. Employing an initially unstressed material, the computation was continued until sufficient material was extruded so that the steady-state extrusion process had fully developed.

Isotropic work hardening based on a measured stress-strain curve from a tension test was utilized in the analysis.

In addition to the area reduction, extrusion through the die generated a distribution of shearing strain across the section. The history of longitudinal stress just under the sheet boundaries exhibited a peak of tensile stress just outside the die and this decreased somewhat to constitute the residual stress. Near the center plane, tensile stresses in the die changed to compressive residual stresses in the product. These features are consistent with the known development of extrusion defects, such as the appearance of surface and internal cracks.

(2) Wave Propagation, Impact and Constitutive Relations

Graduate Students: G. A. Nystrom

R. W. Young

Studies were completed on wave propagation in periodic composites and the effect of heterogeneous material properties on the diffusion of impact energy; also on the thermomechanical coupling effect in the transient deformation of viscoelastic materials. The utilization of bounding theorems in providing estimates of maximum deformation and duration of deceleration following impact was described in reports which have been distributed.

Reference Publications:

1. E. H. Lee, "Some Restrictions on Constitutive Equations", Discussion Paper, Foundations of Continuum Thermodynamics, (Eds. J.J.D. Domingos, M.N.R. Nina and J.H. Whitelaw), 251-256, Macmillan, London, 1974.
2. E. H. Lee, "Wave Propagation in Composites with Periodic Structures", Proc. CANCAM 75, (Ed. G. Dhatt), G49-G59, 1975.
3. E. H. Lee, B. Budiansky, and D. C. Drucker, "On the Influence of Material Properties on Stress Wave Propagation through Elastic Slabs", J. Appl. Mech., 42, 417-422, 1975.
4. E. H. Lee, "Thermo-viscoelasticity", Mechanics of Viscoelastic Media and Bodies", (Ed. J. Hult), 339-357, Springer-Verlag, 1975.
5. R. W. Young, "Thermomechanical Coupling Effect in Transient Deformation", SUDAM Report No. 75-10, 1975.

6. G. A. Nystrom, "Combined Use of Lower Bound Theorems and Available Upper Bound Information for Rigid-Plastic Structures", SUDAM Report No. 75-12, 1975.
7. G. A. Nystrom, "Reciprocal Calculation of Upper and Lower Bounds for Plastic Structures under Impact", SUDAM Report No. 75-13, 1975.
8. E. H. Lee and R. L. Mallett, "Structural Analysis and Design for Energy Absorption in Impact", SUDAM Report No. 75-15, 1975.
9. D. R. Carter, W. C. Hayes, R. L. Mallett and T. M. Wright, "Quasi-static and Impact Tests on Porous Media", SUDAM Report No. 75-16, 1975.
10. E. H. Lee, "The Basis for an Elastic-plastic Code", SUDAM Report No. 76-1, 1976.
11. E. H. Lee, R. L. Mallett and W. H. Yang, "Stress Analysis of Metal-forming Processes", SUDAM Report No. 76-2, 1976.

## 37. STRUCTURE OF DENSE FLUIDS

J.E. Lind Jr., Associate Professor, Chemical Engineering

### Graduate Students:

H. I. Lips\*

C.-L. Lu\*

\*Received Ph.D. during report period.

### Agency Support:

NSF GK 38120

### Technical Objective:

To relate the thermodynamic and transport properties of dense fluids to the structure of the fluid and in particular to understand the effects of long range coulomb fields as well as the strongly directional interactions of hydrogen bonds upon these properties. The effects of these interactions are being examined in three types of comparisons: liquid metals compared to non-metals; and hydrogen bonded fluids compared to nonhydrogen bonded, polar fluids and nonpolar fluids.

### Approach:

Each experimental system of a liquid with strong electrostatic forces or hydrogen bonding between molecules is chosen so that there is also a reference liquid system without these forces, yet with molecules essentially isoelectronic to those in the system with strong interactions. In this fashion the properties of the reference system can be subtracted from those of the liquid with strong intermolecular forces at the same temperature and volume. This difference can be used to test perturbation theories of the liquid state and/or to infer the magnitude of effects which theory cannot yet treat. These experimental perturbations are usually much less sensitive to the detailed structure of the molecules of the reference system, such as their nonsphericity, than are the properties of the reference system itself and so the refer-

ence system can be treated as a simple system such as a system of hard spheres.

A very precise technique for measuring PVT properties permits evaluation of the first and second order configurational derivatives of energy and entropy up to 8 kbars in order that volume and temperature can be easily varied by over 30%. Self diffusion measurements are made under pressure by spin-echo NMR and related to the thermodynamic properties.

#### Research Report:

##### (1) Liquids with Hydrogen Bonded and Dipolar Molecules

The PVT properties of t-butylamine and t-butyl alcohol (2-methyl-2-propylamine and 2-methyl-2-propanol) and neopentane (2,2-dimethylpropane) have been measured and their energies, entropies and thermodynamic configurational properties have been computed. Differences between the properties of amine and the alcohol and properties of the neopentane are compared with the results of a perturbation theory from the hard sphere liquid for hydrogen bonding. A simple square-well perturbation permitting two neighbors to hydrogen bond to each molecule is adequate to represent all the thermodynamic properties of the alcohol and amine. This suggests that the structure of the liquid is dominated by the excluded volume of the molecules rather than by the hydrogen bonds. The hydrogen bond well depth is 5650 cal/mole for the alcohol but only 4500 cal/mole for the amine. A unique feature of strongly hydrogen bonded liquids is the positive value of  $(V/R)(\partial C_v/\partial V)_T$  which is predicted by the theory for the alcohol but not for the amine and agrees with experiment in both cases.

When the theory is applied to an alcohol of the size of water using the same hydrogen bond parameters as for t-butyl alcohol, the energy and entropy cannot both be simultaneously set in agreement with water data that has been adjusted for the loss of half its hydrogen bonds. This suggests that the core of the water molecule is very small

and it is the cooperative interaction of the hydrogen bonds which holds the molecules in positions favorable for hydrogen bonding rather than the excluded volumes of the cores, which provide that function for the t-butyl compounds.

## (2) Thermodynamics of Liquid Metals:

Graduate Student: C.-L. Lu

The PVT-properties of the alkali metals, Na, K, and Rb, have been studied as well as those of gallium and mercury. A model was then used to attempt to calculate these experimental results and thereby determine which interactions are most important to the properties of these metals. A model using pseudopotentials to calculate the ion-electron interactions and a coulomb repulsion with screening to calculate ion-ion interactions was fitted to a single pressure point with one adjustable parameter. Agreement of this model with the experimental compressibilities, kinetic pressure coefficients, and second order volume derivatives of the energy and entropy was excellent for the alkali metals.

The high values of  $(V/R)(\partial S/\partial V)_T$  for mercury suggested the need for ion core-ion core repulsions caused by the overlap of core electrons. While the core-core repulsion potential is not well known, the introduction of it gave the correct trend so that a good fit could be achieved.

For gallium, the unusual property is  $(V/R)(\partial C_V/\partial V)_T$  which is positive as in the case of t-butyl alcohol, while it is negative for all the other liquid metals that were studied. This result suggest that there are strong short-range attractive forces in gallium. If there be two interactions per atom with nearest neighbors, then the hydrogen bond theory can be modified and applied. The theory than suggests a lower bound of 13,000 cal/gm atom for the energy of these interactions as well as a very small volume of interaction compared to a hydrogen bond.

Thus the use of very precise PVT-data which permit the calculation of high order configurational derivatives has lead to pinpoint the need for ion-core repulsions in liquid mercury and short-range attractions in liquid gallium.

Reference Publications:

1. R.F. Cleverdon and J.E. Lind Jr., "Hydrogen Bonding in t-Butyl-Alcohol and Amine and a Water-Like Alcohol," J. Chem. Phys., in press.
2. Harold I. Lips, "Self-Diffusion in Liquids: Relation to Thermodynamic Properties and Effect of Strong Interactions," Ph.D. Thesis, Stanford University, Stanford, CA, July 1975.
3. Cheng-Liang Lu, "Energy and Entropy Contributions to the Thermodynamic Properties of Liquid Metals," Ph.D. Thesis, Stanford University, Stanford, CA, November 1975.

### 38. SUPERCONDUCTIVITY AND MOLECULAR PHYSICS

W. A. Little, Professor of Physics

#### Professional Associates:

H. Gutfreund

R. Lorentz

M. Belombe

#### Graduate Students:

J. W. Brill\*

M. Novotny

\*Received MS during report period.

#### Agency Support:

NSF/MRL through CMR

NSF GH 41213

NASA JPL 953752

NASA NGL 05-020-242

Research Crop.

#### Technical Objective:

To study the feasibility of obtaining superconductivity at a relatively high temperatures in organic and organo-metallic systems. To develop means for detecting the presence of molecules by structure specific sensing techniques. To understand how information may be imprinted and recalled in a neural network.

#### Approach:

Our main line of work is the study of the possibility of high temperature superconductivity using an exciton induced electron-electron interaction rather than the phonon mechanism. Our efforts have centered on linear chain systems where we believe a sufficiently strong excitonic interaction can be obtained with suitable ligands.



We have completed a calculation of the  $T_c$  of a particular class of metal-organic system which, if they could be synthesized, would appear to be high temperature superconductors.<sup>(1)</sup> Furthermore, we show how they can be prepared so that the superconducting state would be favored over the Peierls' state, and, that in these particular systems the, so called, Migdal approximation which neglects higher order corrections to the electron-exciton vertex is a good approximation. Preliminary work on the synthesis of the ligand systems has yielded a new class of anion-cation linear chain compounds.<sup>(2)</sup>

Work has continued on the fluorescent immuno-assay technique which was developed under CMR support. A patent has been awarded to the University and the rights to it have been licensed to a major bio-medical diagnostic company for development as a commercial instrument.

Further progress has been made in the study of memory in neural networks.<sup>(3)</sup> An exact solution to the problem of the storage capacity of the network has been derived for a particular class of network. This shows that cyclic persistent patterns are needed as an active representation of stored information if the full storage capacity of the network is to be utilised. An experimental search for such patterns is being proposed.

#### Reference Publications:

1. D. Davis, H. Gutfreund and W. A. Little, "Proposed Model of a High Temperature Excitonic Superconductor," Phys. Rev. B (to be published) June (1976).
2. W. A. Little and R. Lorentz, "Solid Bis(1,10-phenanthroline)platinum(II)-and Bis(2,2'-bipyridyl)platinum(II)Platinates(II) with Intermolecular Metal-Metal Interactions," Inorganica Chimica Acta, Vol. 18 No. 3, (1976).
3. W. A. Little and G. L. Shaw, "A Statistical Theory of Short and Long Term Memory," Behavioral Biology, 14, 115-133 (1975).

39. EXPERIMENTAL AND THEORETICAL STUDIES ON ROCK-FORMING SYSTEMS AT HIGH  
TEMPERATURES AND PRESSURES

W. C. Luth, Associate Professor, Geology

Professional Associate

P. M. Fenn, Research Associate, Geology

Graduate Students

M. Naney

Agency Support

NSF GA 41731 (With W.A. Tiller and G.E. Brown)

Technical Objective

Experimental simulation, and analysis, of rock-forming processes taking place in the Earth's crust (outer 35 km) and upper mantle which involve interaction with, and crystallization from, silicate liquids in the presence, or absence, of an aqueous field phase.

Research Report

(1) Growth of Albite from Hydrous Silicate Melts.

P. M. Fenn

Albite ( $\text{NaAlSi}_3\text{O}_8$ ) is the sodium end-member of the ternary feldspar group. These minerals, plagioclase (Ca-Na) and alkali feldspar (K-Na), show extensive solid solution and are the most abundant minerals of the earth's crust. Experimental studies of the phase equilibria and the kinetics of nucleation and growth of albite from hydrous melts in the system  $\text{NaAlSi}_3\text{O}_8$ - $\text{SiO}_2$ - $\text{H}_2\text{O}$  are currently in progress. The effects of the redistribution of  $\text{SiO}_2$  and  $\text{H}_2\text{O}$  on both the growth kinetics and crystal morphology are of special interest.

(2) Phase Equilibria in Silicate- $\text{H}_2\text{O}$  Systems; Volume Relations.

Analysis of available experimental P-V-T-Composition data on the system  $\text{NaAlSi}_3\text{O}_8$  clearly demonstrates the necessity for explicit consideration of volume as a process variable in treating crystallization and melting relationships in natural systems. Most applications of experimental data to geologic systems involve an implicit assumption

that the volume of the system is determined by the pressure (depth), temperature, and composition variables. If the volume of the system is constrained by the environment of crystallization (or melting) then estimates of the depth at which these processes occur in the natural environment, based on a variety of mineral equilibria, may be in error by 1-15 km.

(3) Crystallization of Ferro-Magnesian Phases from Granitic Liquids.

M. Naney

Biotite and hornblende are the common ferromagnesian phases found in the granitic rocks. Experimental studies on phase equilibria and kinetics of these phases from granitic liquids containing dissolved  $H_2O$  are continuing. These phases crystallize from liquids which are either saturated with, or undersaturated with, an aqueous fluid phase over a wide range of pressure and temperature. Consequently the presence of these hydrous, ferro-magnesian, phases in granitic rocks does not imply the necessary existence of an aqueous fluid phase at the time of crystallization.

Reference Publications:

- Fenn, P.M., "The effect of pressure on the monoclinic alkali feldspar lattice" (abstr.). EØS, Trans. Amer. Geophys. Union, 56, 1077, 1975.
- Fenn, P.M., "The nucleation and growth of sodium-rich alkali feldspars from hydrous melts in the systems  $NaAlSi_3O_8$ - $KAlSi_3O_8$ - $H_2O$  and  $NaAlSi_3O_8$ - $SiO_2$ - $H_2O$ " (abstr.). Prog. with Abstracts, 1, Geol. Assoc. Canada/Mineral. Assoc. Canada Ann. Meet. Edmonton, Alberta, 65, 1976.
- Long, P.E., and W.C. Luth, "Genetic Implications of Ba zoning in microcline megacrysts from Precambrian granitic rocks of the Dixon-Penasco area, Northern New Mexico" (abstr.). Abstr. with Prog. 7 Geol. Soc. Amer. Ann. Meet. Salt Lake City, Utah, 1176, 1975.
- Luth, W. C., "Specific volume as a system variable in treating crystallization of silicate- $H_2O$  systems" (abstr.). Abstr. with Prog., 7, Geol. Soc. Amer. Ann. Meet. Salt Lake City, Utah, 1180, 1975.
- Naney, M.T., "Nucleation and growth of biotite and clinopyroxene from haplogranitic magmas" (abstr.). EØS, Trans. Amer. Geophys. Union, 56, 1075, 1975.

#### 40. REACTIVITY OF SOLIDS

R. J. Madix, Associate Professor, Chemical Engineering

##### Graduate Students:

N. M. Abbas	I. E. Wachs
S. W. Johnson	D. Ying
D. Y. Ngan	

##### Agency Support:

NSF/MRL through CMR  
ACS Petroleum Research Foundation  
Research Development Fund  
NSF Materials Division  
NSF Chemical Processes Division

##### Technical Objective:

To elucidate the chemical kinetics and mechanisms of reactions at the gas-solid interface and the influence of surface structure and composition thereon.

##### Research Report:

##### (1) High Temperature Reactions of Solids

Graduate Student: D. Ngan

Molecular beam, low energy electron diffraction and electron microscopic techniques are being utilized to elucidate the kinetics and reactive collision processes occurring in high temperature gas-solid reactions. In particular, reactions were studied in which the reaction products vaporize. These products were detected mass spectrometrically. The reactant gas was directed at the surface under study in the form of a modulated molecular beam, the products and the scattered reactant beam were phase-sensitively detected or the product waveform was observed. The product phase lag is directly related to the kinetic rate constant. Thus, the reaction sequence occurring on the surface can be elucidated.

The oxidation of molybdenum with chlorine and oxygen-chlorine mixtures was studied extensively. Both lock-in phase and amplitude measurements and waveform analysis methods on the desorbing products were employed to understand the reaction process. The reaction

sequence was complex, involving simultaneous solution of chlorine in the molybdenum and surface diffusion of oxygen. The mechanism of the oxychlorination was similar to that observed for the chlorination reaction alone. The reaction clearly involves two separate branches one of which appears to be the result of a surface phase change.

(2) The Effect of Surface Composition and Structure on Catalytic Decomposition

Graduate Students: S. Johnson  
N. Abbas  
D. Ying

The primary objective of our research is to understand the role of surface compounds and structures on product selectivity, surface decomposition kinetics, sticking probabilities and inhibition by product species. Our approach is to use ultra-high vacuum methods for characterizing the above features of the surface reactivity; namely, we are employing Auger-Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED), work function measurements, and flash desorption methods. We also wish to extend our studies to include ultraviolet photoemission spectroscopy. It is only fair to say that the connection between this type of work and "Practical" catalysis is now unclear, but our work is conducted with this connection in mind. Our results to date indicate that these methods have great potential for studying fundamental problems in the catalytic conversion of coal gas to methane and methanol.

The decomposition of formic acid was studied on partially oxidized Ni(110) surfaces, prepared by exposing the clean surface to as much as 10L O<sub>2</sub>. While the autocatalytic mechanism producing H<sub>2</sub> and CO<sub>2</sub> previously observed on the clean surface, persisted for oxygen exposures of less than 10L, its peak position, therefore its kinetic parameters, was altered, and a second, non-autocatalytic process was introduced. After 10L oxygen exposure, the autocatalytic step was not observed. Carbon monoxide was produced from an adsorbed CO species, as with the clean surface, although its peak

position suggested a partial reduction of the oxidized surface as the decomposition reaction proceeded. The results of this investigation suggest that oxygen adsorbed on the Ni(110) surface exists as both surface and sub-surface species. The latter has a ligand effect which preserves the metallic behavior of the clean surface while altering the kinetic parameters. This study is still in progress and will be extended to formic acid decomposition on partially oxidized Ni(100) and Ni(111) surfaces.

The study of formic acid ( $\text{HCOOH}$ ) decomposition on Ni(110)(2x1)C was extended to the case of  $\text{D}_2$  formation. It displayed second-order kinetics with a coverage dependent pre-exponential factor,  $\nu_2$ . A low value for  $\nu$  was observed suggesting the presence of trapping sites on the surface. Studies are currently being performed so as to achieve both a qualitative and quantitative understanding on the recombination of deuterium atoms in the presence of the formate intermediate on this surface and also on Cu(110). We have also conducted experiments on  $\text{CO}_2/\text{HCOOH}$  on a Ni surface of varying carbide coverage. The purpose of this study was to obtain an understanding of how carbon affects the nickel surface environment as the amount of carbon is increased incrementally. The explosive peak, observed on the 'clean' surface, decreased in amplitude; while the broad peak, observed on the 'carbide' surface, increased in amplitude with increasing carbon coverage. This indicated that carbon atoms (in the form of islands of carbide) blocked the pathway for the decomposition on the clean nickel surface and at the same time created carbide decomposition sites.

Lastly, the formic acid decomposition was studied on Cu(110) and Ni/Cu(110) alloy surfaces with different surface compositions. (50% Ni, 50% Cu; 65% Ni, 35% Cu; 80% Ni, 20% Cu). For the Ni/Cu(110) alloy, as surface Ni increases, its catalytic properties start to deviate from the Ni(110)(4x5)C surface; the selectivity for the carbon monoxide production becomes compatible to carbon dioxide and hydrogen production. This demonstrates the importance of surface

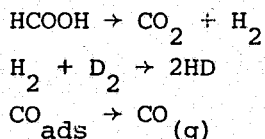
compositional changes to the selectivity of decomposition paths of formic acid.

Furthermore, the decomposition of acetic acid was studied on Ni(110) (4x5)C, Ni/Cu(110) alloy surface (with different surface compositions), and Cu(110). In general, the decomposition of acetic acid qualitatively follows a systematic trend as observed for the decomposition of formic acid on these surfaces. The research is still in progress.

### (3) Molecular Beam Relaxation Spectrometry

Graduate Student: I. Wachs

The time response function observed for product molecules emitted from a solid surface from a square wave of reactant incident on the surface carries information about the surface reaction mechanism (reaction transform function). We were able to obtain waveforms for several reactions including



as well as phase and amplitude information necessary to allow kinetic analysis. The exciting feature of this work is that it allows visual display of the surface transform function as the experiment is in progress, thus allowing the experimenter to find interesting regions of temperature and pressure for further quantitative study quite easily. It also opens up the possibility of waveform analysis for studying the kinetics and mechanism of reactions on well-defined surfaces.

The interaction of formic acid with a (110) oriented nickel crystal has been studied over the temperature range 175-950°K with molecular beam relaxation spectrometry (MBRS). At temperatures below 300°K no decomposition of formic acid occurred; and formic acid simply adsorbed and desorbed with a finite surface residence time. Approximately 95% of the formic acid was decomposed by the Ni(110) catalyst between 300-400°K; the modulated reaction products ( $\text{CO}_2$ , CO,  $\text{H}_2$  and

H<sub>2</sub>O) began to appear at circa 400°K.

The products were formed by a sequential mechanism, since phase-lags greater than 90 degrees were observed. The phase-lags of H<sub>2</sub> and H<sub>2</sub>O were much greater than those for CO and CO<sub>2</sub>. This behavior reflects the additional time necessary for the recombination of surface radicals in the formation of the products H<sub>2</sub> and H<sub>2</sub>O. Since the phase-lags for all of the products were different, they were not produced by a single rate-limiting step. Excellent agreement was obtained between the proposed mechanism and the observed experimental results. These studies reveal interesting features in the kinetics of elementary reaction steps on surfaces.

#### Publications:

1. (with Falconer, J.) "Surface Stabilized Reaction Intermediate: Formic Anhydride." Published as a "Letter to the Editor" Surface Sci. 51/2, 546-548 (1975).
2. (with Helms, C. R.) "Molecular Beam Relaxation Spectrometry (MBRS) Measurement of Desorption Rate Constant for CO on Ni(110)." Surface Sci. 52, 677 (1976).
3. (with Falconer, J. and Suszko, A.M.) "The Autocatalytic Decomposition of Acetic Acid on Ni(110)." Surface Sci. 54, 6, (1976).
4. (with McCarty, J.) "Formic Acid Desorption from Graphitized Ni(110)." Surface Sci. 54, 210 (1976).
5. "Catalytic Reactions on Metal Surfaces: A Review of the Recent Contributions of Surface Science." J. Vac. Sci. Technol., 13, No.1, Jan/Feb. 1976.



#### 41. ELECTROCATALYTIC STUDIES EMPLOYING SOLID-STATE OXIDE ELECTROLYTES

D.M. Mason, Professor, Chemical Engineering and Chemistry

##### Graduate Students:

J.C. Chapman  
I.-S. Shaw\*

J.C. Wen  
M. Yamada\*

\*Received M.S. during report period.

##### Agency Support:

National Science Foundation through Dept. of Chemical Engineering

##### Technical Objective:

To study experimentally the catalytic processes involved in electrocatalytically decomposing NO to the elements ("the catalytic muffler reaction") employing the family of solid oxides electrolytes having large oxygen ion conductivities (e.g.  $ZrO_2$  stabilized with CaO,  $Sc_2O_3$ , etc.). Also to study the electrocatalysis of oxidation of coal gas constituents ( $CO$ ,  $H_2$ ,  $CH_4$ , etc.) employing these solid electrolytes as fuel-cell components. There is a focus on studying catalytic behavior of oxide candidates that display high oxygen conductivities at more moderate temperatures (500-700°C) than zirconia (ca. 1000°C); e.g.  $Bi_2O_3$ ,  $GdO$  and  $CeO_2$ . It is being planned to measure the thermodynamic properties of these latter compounds.

##### Research Report:

In continuing the investigation this year techniques for controlling the surface morphology of the electrode materials coating the electrolyte have been developed. The interest in controlling the morphology of the surface arose in the studies of NO electrolytic decomposition where it was found that a randomly porous platinum electrode configuration gave rates of decomposition about 100-1000 times larger than non-porous platinum electrodes (D.M. Mason, S. Pancharatnam and R.A. Huggins, "Catalytic Decomposition of Nitric Oxide on Zirconia by Electrolytic Removal of Oxygen," J. Electrochem. Soc. 122, 869-875, 1975). This behavior

was hypothesized to be due to the electrochemical creation of F-centers in zirconia which are highly catalytic towards NO dissociation. To test this hypothesis it is necessary to produce a well-defined electrode geometry where the area of electrode-to-electrolyte surface exposed to the reacting system can be varied. Rectangular grids with different mesh sizes have been constructed employing photo-etching techniques that permit surface ratios of exposed electrolyte to electrode to vary by a factor of as much as 100. At present platinum and gold grids have been constructed--platinum being catalytic, gold non-catalytic with respect to NO decomposition.

Initial studies with the fuel-cell systems  $H_2$  and CO with scandia-stabilized zirconia and platinum electrodes have indicated that around  $700^\circ C$  the air-cathode is kinetically limiting compared to the fuel anode. This phenomenon is being further studied by varying the electrode catalysts.

#### Reference Publications:

1. D.M. Mason, S. Pancharatnam and R.A. Huggins, "Catalytic Decomposition of Nitric Oxide on Zirconia by Electrolytic Removal of Oxygen," J. Electrochem. Soc. 122, 869-875 (1975).
2. D.M. Mason and Phil E. Depoy, "Periodicity in Chemically Reacting Systems: A Model for the Kinetics of the Decomposition of  $Na_2S_2O_4$ ," Faraday Symposia of the Chemical Society, 9, 47-54 (1975).
3. D.M. Mason and Boo Goh Ong, "Numerical Solution of Equations Arising in Energy Transport in Nonequilibrium Chemically Reacting Systems," Chem. Eng. Sci. (1976).

## 42. EPITAXIAL CRYSTAL GROWTH

B. L. Mattes, Senior Research Associate, Center for Materials Research

### Professional Associates:

R. H. Bube  
A. G. Elliot  
R. S. Feigelson  
G. L. Pearson  
D. A. Stevenson

### Graduate Students:

S.-H. Chiao  
H. Dun  
Y. M. Houn  
E. Jones  
P. K. Vasudev

### Agency Support:

ARO DAHC04-74-C-0025  
NSF/RANN AER 74-13036  
ONR N00014-67-A-0112-0082  
Rockwell International F-19628-74-C-0038  
NSF/MRL through CMR

### Technical Objectives:

To grow high quality epitaxial layers for characterization measurements and device applications, and to study homo- and heteroepitaxial nucleation and growth processes.

### Approach:

An interdisciplinary approach, based primarily on the liquid phase epitaxial growth of GaAs, is being used to study nucleation and growth, and impurity incorporation and their effects on electrical transport properties.

### Research Report:

The above objectives are being achieved with considerable feedback between the following programs (listed by each principal investigator):

- (I) Control of Impurities in the Epitaxial Growth of High Quality GaAs  
(Principal Investigator: D. A. Stevenson; Graduate Student: H. Dun)
- (II) Growth and Properties of Semi-Insulating Epitaxial GaAs  
(Principal Investigator: G. L. Pearson; Graduate Student: Y. M. Houngh)
- (III) Investigation of Deep Impurity Levels in GaAs by Photocapacitance and Related Techniques  
(Principal Investigator: R. H. Bube; Graduate Students: S.-H. Chiao, P. K. Vasudev)
- (IV) Thin Film Gallium Arsenide for Low Cost Photovoltaic Solar Energy Conversion  
(Principal Investigator: D. A. Stevenson; Research Associate: A. G. Elliot; Graduate Student: E. Jones)

All GaAs synthesis is carried out in the Epitaxial Growth Facility (CMR Central Facilities) under the direction of Dr. Brenton Mattes. In the following the interrelation of these programs is emphasized, showing the role each has in the attainment of the overall Technical Objective.

The use of GaAs for microwave devices and solar cells has required quite different, but growth related solutions to two problems: (a) impurity control and (b) thin epitaxial layers on inexpensive substrates, respectively. Programs I, II, and III are interrelated and directed to determine the source and identity of the impurities in the growth system, to control the impurities during growth, and to characterize these impurities in the epitaxial layer. All of these programs have made significant progress in the understanding of impurities and their effect on the growth and the electrical properties of the layers. The solubility of impurities in the layer appears to be related to the formation of GaAs clusters at the liquid-solid interface and to the formation and dissociation of impurity complexes in the liquid. In order to achieve semi-insulating GaAs (II), for example, shallow donors and acceptors must be self-compensated and Cr must be incorporated to form deep trapping levels. Without self compensation Cr, with a lower oxidation state than Si and C in the Ga melt, reduces

the oxides of Si and C, and they are then incorporated as shallow donors and acceptors in the layer. Semi-insulating layers that act as a buffer between an active layer and the substrate, and as a medium for ion implantation have improved the characteristics for field effect transistor applications. Reproducible growth of semi-insulating GaAs layers has been related to the effects of chemical reactions between the growth system components ( $\text{SiO}_2$ , C,  $\text{H}_2$ ) which result in inclusion of impurities that can be identified in the ambient atmosphere above the Ga-melt (I) and, in addition, identified by photocapacitance, photoluminescence, thermally stimulated capacitance and related techniques (III).

All of these studies in conjunction with nucleation and growth studies of epitaxial GaAs and other materials have led to a "building block" model for crystal growth. For GaAs, the "block" appears to be a cluster of 848 Ga and As atoms in the form of a rhombic dodecahedron bounded by  $\{110\}$  planes. These clusters have been deduced from shadowed high resolution replicas in a TEM. Their size and shape is stable based on Madelung energy calculations, completed dangling bonds on the surface, and stoichiometry. Crystal growth, therefore, appears to be the stacking of these "blocks" to lower differences in the completed dangling bond energy at their apexes. The stacking tendency when the interface is Ga stabilized is to form  $\{111\}$ B hillock surfaces on all substrate orientations and on all growth, etched and cleaved surfaces. This can explain the superlattice structures that have been observed in LEED patterns. In heteroepitaxial growth on oxide substrates (IV) nucleation and growth appears to be limited by the ability of the growth technique to raise the supersaturation of the As at the interface to that necessary for cluster formation, and secondly, by the lattice match and reactivity between the substrate and the layer material.

Impurities appear to be incorporated into the layer when an additional layer of Ga and As atoms attach to the crystal interface and diffuse between the clusters as the blocks stack together during growth. On the surface of the cluster the more active completed 1st

nearest neighbor dangling bonds will probably break to accommodate these atoms while the more stable 2nd nearest neighbor bonds will stabilize intrinsic vacancy sites. The substitutional impurity solubility is primarily limited to the available sites in this added layer ( $\sim 19\%$  of the total atoms in the crystal). In general, only a fraction of these sites will accommodate impurities and they are related to the reactivity of the "block's" apexes. Therefore, typical solubilities between  $10^{19}$  and  $10^{20}$  atoms per  $\text{cm}^3$  are found in GaAs. These values may vary, however, with the size and electronic structure of the impurity and the presence of other impurities.

#### Reference Publications:

1. B. L. Mattes, Y.-M. Hounq and G. L. Pearson, "Growth and Properties of Semi-Insulating Epitaxial GaAs", J. Vac. Sci. Technol. 12, 89 (1975).
2. B. L. Mattes, "Liquid-Solid Interfaces During Epitaxial Nucleation and Growth of III-V Compounds", Crit. Rev. Solid State Sci. 5, 457 (1975).
3. P. K. Vasudev, B. L. Mattes, E. Pietras and R. H. Bube, "Excess Capacitance and Non-Ideal Schottky Barriers on GaAs", Solid State Electronics 19, 557 (1976).
4. B. L. Mattes, "Atom Clustering and Stacking Formations on Interfaces", J. Vac. Sci. Technol. 13 (1976).

43. **PHYSICAL CHEMISTRY OF LIPID, LIPID-PROTEIN OR LIPID-DETERGENT BILAYER MEMBRANES**

**H. M. McConnell, Professor, Chemistry**

**Professional Associates:**

**P. Brulet\***  
**G.M.K. Humphries**  
**P. Kury**  
**J.T. Lewis**  
**J. Murdoch**  
**P. Rey**  
**J. Van der Bosch**

**Graduate Students:**

**B.R. Copeland**  
**J.T. Lewis**  
**E.J. Luna**  
**A.H. Ross**  
**M.A. Schwartz**  
**J.R. Sheats**  
**D.D. Thomas\***

**Undergraduate Student:**

**A. Kawamoto**

**\* Received PhD during report period.**

**Agency Support:**

**NSF BMS 75-02381**  
**NSF BMS 75-02381 A01**  
**ONR N00014-75-C-0869**  
**NIH AI13587-01**

**GM-07026-01 (Humphries and Kury)**

**Technical Objective:**

**The aim of this research is to attain a more thorough understanding of the structure and function of biological and synthetic membranes.**

## **Approach:**

Various physical-chemical techniques such as electron spin resonance (ESR), freeze-fracture electron microscopy and two-dimensional gel electrophoresis are used to study the physical nature and chemical composition of biological membranes.

## **Research Report:**

### **(1) Immunochemistry**

#### **(A) Characterization of natural lymphocyte membranes.**

Professional associate: P. Kury

We are isolating the plasma membrane from different classes and subclasses of lymphocytes and characterizing the physical nature and number of cell surface antigens on these membranes. Principally we are interested in cell-cell recognition where a physical interaction between two cells can trigger biochemical events inside a cell. The method of two-dimensional electrophoresis coupled with precipitation with specific antisera is being used to characterize these membrane proteins.

#### **(B) Immunochemistry of artificial bilayers.**

Professional associates: G.M.K. Humphries  
P. Brulet  
P. Rey  
J. Murdoch

We are presently working on establishing the physico-chemical factors that are essential for the elementary steps of the immune response. We are using liposomes, which are lipid bilayers of which one can change the composition and therefore affect the microviscosity of the membrane. This study involves the synthesis of a wide variety of lipid haptens where the hapten is the nitroxide spin-label group. Several monovalent and divalent haptens have been synthesized and



and studied. We have also isolated and purified specific bivalent antibodies against one hapten using different chromatographic methods. So far we have studied to some extent the specific binding of the antibody to the membrane haptens and the complement fixation under a wide variety of physico-chemical conditions.

## **(2) Reconstitution of Membrane Proteins**

### **(A) Microfilament protein-spectrin.**

Graduate student: E. J. Luna

Spectrin is a large filamentous protein which underlies the membrane of the human red blood cell. Its physical properties in solution and the interrelationships between spectrin, phospholipids and other erythrocyte membrane components are being studied by ESR and freeze-fracture electron microscopy.

### **(B) Anion channel.**

Graduate student: A. H. Ross

We are isolating and reconstituting components of the erythrocyte membrane in order to better understand the mechanism of action of membrane proteins in general.

## **(3) Physical State of Membranes and Micelles**

### **(A) Phase diagram of neutral and negatively charged phospholipids.**

Graduate student: E. J. Luna

Phase diagrams were determined for binary mixtures of L- $\alpha$ -dipalmitoylphosphatidylserine and dipalmitoyl and dimyristoyl phosphatidylcholines. These phase diagrams provide evidence for compound formation in phospholipid systems.

**(B) Cholesterol effect on immunogenicity.**

Undergraduate student: A. Kawamoto

While in this laboratory, G.M.K. Humphries showed an increase in complement fixation for mixtures of phosphatidylcholines and cholesterol when the cholesterol concentration was raised above 35 mole %. As a preliminary to the study of the immunogenicity of a membrane glycoprotein in various lipid matrices, conditions necessary for the incorporation of glycophorin into phospholipid mixtures containing greater than 35 mole % cholesterol are being determined.

**(C) Phospholipid-detergent phase diagram and induced membrane asymmetry.**

Graduate student: M. Schwartz

Two studies are presently underway. First, a phase diagram of phospholipids with detergent is being studied using a spin-labeled detergent, in order to find the phase boundary between the micelle and vesicle states for phospholipid-detergent systems. Second, the asymmetry between inner and outer layers in phospholipid vesicles is being investigated by attempting to find a system where composition asymmetry exists in large vesicles, then investigating its structural and thermodynamic properties.

**(D) Cell-mediated immune response.**

Graduate student: J.T. Lewis

Since the discovery by Humphries and McConnell that complement-mediated attack on model phospholipid membranes depends strongly on the cholesterol content of the membrane (PNAS 72, #7, 2483 (1975)), studies have been initiated to determine under what conditions "killer" lymphocytes will attack model target membranes. Distribution of antigens in the plane of the membrane is investigated by freeze-etch electron microscopy.

(E) Diffusion of phospholipids in membranes.

Graduate student: J. Sheats

I am currently designing an experimental technique for the accurate measurement of diffusion coefficients of spin-labeled molecules in oriented multi-lamellar phospholipid bilayers. The spin labels in specified regions of the bilayers will be reduced photochemically, by the alkyl radicals generated from alkyl pentacyanocobaltate complexes, and the diffusion of the remaining spin labels can then be followed by ESR. The chemistry has been developed, and the physical techniques are now being worked out.

(F) Theoretical studies in 2nd order phase transitions.

Graduate student: B. Copeland

I have been investigating a number of theoretical models for phase transitions - particularly 2nd order phase transitions. Most of this work uses either Landau 2nd order Phase Transition Theory or Lattice Order-Disorder Transition Theory. The work is directed at development of stronger physical intuition about 2nd order transitions, and application of such intuition to biological systems.

(G) Fusion of phospholipid vesicles induced by concanavalin A.

Professional associate: J. Van der Bosch

The temperature dependence of fatty acid spin-label resonance spectra and freeze-fracture micrographs of sonicated dipalmitoyl-phosphatidylcholine vesicles in the absence and presence of concanavalin A demonstrate a strong interaction of concanavalin A with these lipid membranes, which results in fusion of the vesicles. A pronounced maximum in the rate of fusion is found at  $36^{\circ}$ , the midpoint of the phase transition range of the vesicles. This maximum has been interpreted to be due to structural fluctuations, which are maximal in the phase transition range of the membranes.

#### (4) Development of ESR

##### (A) Slow motion studies by ESR.

Graduate student: D.D. Thomas

A technique called saturation transfer ESR has been developed to follow slower motions of spin labels than normal ESR. The accessible time range is  $10^{-7} \leq \tau_2 < 10^{-3}$  sec where  $\tau_2$  is the rotational correlation time. This method has been applied to study the motion of myosin, a protein of the muscle.

#### Reference Publications:

1. Gillian M. Kitch Humphries and H. M. McConnell, "Antigen Mobility in Membranes and Complement-Mediated Immune Attack", PNAS 72, 2483 (1975).
2. Philippe Brulet and H.M. McConnell, "Kinetics of Phase Equilibrium in a Binary Mixture of Phospholipids", Am. Chem. Soc. 98, 1314 (1976).
3. W. Kleemann and H.M. McConnell, "Interactions of Proteins and Cholesterol with Lipids in Bilayer Membranes", BBA 419, 206 (1976).
4. Jurgen van der Bosch and H.M. McConnell, "Fusion of Dipalmitoylphosphatidyl-Vesicle Membranes Induced by Concanavalin A", PNAS 72, 4409 (1975).
5. Philippe Brulet and Harden M. McConnell, "Protein-Lipid Interactions: Glycophorin and Dipalmitoylphosphatidylcholine", Biochem. & Biophys. Research Commun. 68, 363 (1976).
6. Gillian M. Kitch Humphries and Harden M. McConnell, "Antibodies Against Nitroxide Spin Labels", Biophys. J. 16, 275 (1976).
7. Philippe Brulet, G.M.K. Humphries and H.M. McConnell, "Immunochemistry of Model Membranes Containing Spin-Labeled Haptens", Nobel Symposium, Skovde, Sweden, to be published.

44. INTEGRATED ELECTRONICS

J.D. Meindl, Professor, Electrical Engineering

Professional Associate

J.D. Plummer

Graduate Students

M.D. Pocha\*

B. Scharf

\* Received Ph.D. during report period

Agency Support

NSF ENG 74-18419

NIH 1 P01 GM1 17940-5

Technical Objective:

To investigate new materials, structures and processing techniques for improving the performance of monolithic integrated circuits; novel biomedical applications of these devices are of particular interest. Many of these biomedical systems employ transducers (piezoelectrics are one example) which require high voltage integrated circuits to drive them. Integrated circuits of this type are not available from commercial manufacturers and hence custom integrated circuits with unusual properties are required.

Approach:

The high voltage integrated circuits required in many biomedical systems employing transducers of a piezoelectric or other nature, are not available commercially primarily for two reasons. First, a good

high voltage MOS transistor has not been readily available. Second, unwanted parasitic interactions between devices at high voltage levels have hampered the integration of many devices in a monolithic substrate. Solutions to both these problems have been found and a new high voltage integrated circuit technology has been developed.

#### Research Report:

In recent years progress in the development of high voltage integrated circuits has not been nearly as rapid as advances in the packing density, chip size, speed, power drain and cost of more conventional circuits. This is not so much because of lack of applications for such circuits, but primarily because of device limitations and because of interaction problems which arise when many high voltage devices are placed together in a monolithic substrate. The purpose of this research is to investigate the fundamental limits of high voltage devices and integrated circuits and to apply this knowledge to the fabrication and characterization of several types of high voltage devices and circuits.

High voltage circuits must either operate at relatively low current levels or utilize some sort of complementary MOS or bipolar configuration if they are to consume reasonable amounts of power. The first approach generally implies slow speed and large resistor values, both of which are unattractive. For these reasons, we have concentrated on developing and modeling a high voltage complementary technology [1]. The most attractive complementary technology is complementary MOS or CMOS because of its relative ease of fabrication and its versatility.

Virtually all commercially available CMOS integrated circuits operate with maximum supply voltages of 15 to 20 volts. The technology which we have developed has pushed the operating voltage of these circuits to in excess of 200 volts. This represents an order of magnitude improvement. This technology is described briefly below.

The N channel component in this CMOS technology is a double-diffused or DMOS transistor. These devices are fabricated by sequentially diffusing first boron and then phosphorus through the same oxide cut. In this manner, an MOS device with a very short channel (typically  $2.5\mu$ ) can be reproducibly built. The short channel provides high transconductance and fast switching capability. The high voltage capability is a result of an  $N^-$  drift region between the device channel and the  $N^+$  drain diffusion.

The high voltage P channel component used in this technology consists essentially of two devices in series which effectively divide the applied voltage. The P channel structure also utilizes an unusual metallization pattern to minimize some of the problems associated with these high voltage devices.

A Ph.D. dissertation [2] completed recently has contributed substantially to our understanding of high voltage devices and the design, fabrication and modeling of high voltage integrated circuits. The dissertation presents an experimental and theoretical study of the DMOS structure (the N channel component used in our CMOS circuits). It examines the electrical parameters of importance in high voltage switching applications, relating these electrical parameters to processing, structural,

and material parameters. It also discusses the optimization of device structures and processing to obtain desired electrical behavior.

The important electrical parameters which are discussed in this dissertation are threshold voltage, breakdown voltage, on resistance, current handling capability and parasitic capacitances from drain-to-substrate and drain-to-source. These electrical parameters are examined in detail and related to device processing and device structure.

Finally, a new device model suitable for computer aided design has been developed that accurately predicts the current-voltage behavior of high voltage DMOS devices over a wide range of operating conditions.

In summary, the significant accomplishments of this past year are the following:

1. New high voltage structures for both P and N channel MOS transistors have been designed, modeled and fabricated.
2. These new transistor structures have been used to realize a complex CMOS integrated circuit which operates with a supply voltage in excess of 200 volts. This circuit has been used to drive a number of transducers and is suitable for driving high voltage displays as well.
3. The N channel DMOS transistor used in these CMOS circuits has been the subject of a comprehensive study. A new model of the device suitable for computer aided design has been developed and the electrical parameters of the device have been related to processing, structural and material parameters.

- [1] Plummer, J.D. and Meindl, J.D., "A Monolithic 200 Volt CMOS Analog Switch," International Solid State Circuits Conference, Feb 1976, Conference Digest, pp. 214-215.
- [2] Pocha, M.D., "High Voltage Double Diffused MOS Transistors for Integrated Circuits," Technical Report 4956-1, Stanford Electronics Labs, March 1976.



45. RELATIONS BETWEEN CRYSTALLINE IMPERFECTIONS AND THE PHYSICAL PROPERTIES OF CRYSTALS

William D. Nix, Professor, Materials Science and Engineering

Graduate Students:

M. A. Burke	R. W. Lund*
K. P. Fuchs**	G. M. Pharr
J. C. Gibeling**	J. W. Sliwa
P. S. Gilman	J. R. Spingarn
S. H. Goods**	C. J. Wei
J. H. Holbrook*	

\* Received Ph.D. during report period

\*\* Received MS during report period

Agency Support:

ERDA E(04-3) 326 PA-17

NSF DMR 75-15477

AFOSR-73-2434

EPRI 7Ps 76-622

NSF/MRL through CMR (Thrust Program on Finite Element Analysis of Inhomogeneous Plastic Deformation in Collaboration with E. H. Lee, D. M. Barnett and O. D. Sherby)

Technical Objective:

To understand and exploit the relation between imperfections and the physical properties of crystalline solids. To develop techniques for predicting and controlling the mechanical and electronic behavior of crystalline materials in order to establish guidelines for making both structural and electronic materials.

Approach:

To carry out both theoretical and experimental investigations of crystalline solids with known concentrations of various types of defects.

Research Report:

- (1) Development of Computer Codes Which can Simulate Finite Plastic Deformation of Materials.

Graduate Student: M. A. Burke

The recent advances in the development of both high speed/large

memory computers and the finite element method of discrete numerical analysis now permits the study of many aspects of material behavior heretofore impossible due to the complex non-linear nature of the mathematical models.

Our efforts with these newly acquired analytical tools have been concentrated mainly on the development of computer codes which can simulate finite plastic deformation of materials. The purpose is to study ductile modes of failure. Two codes have been written for different types of material response. One is capable of simulating non-linear viscous strictly incompressible deformation. At sufficiently high temperature metals and metal alloys deform in this time dependent manner. A second code was developed to simulate finite time independent elastic-plastic deformation. Most ductile materials deform in this manner at room temperature.

Both codes are currently being used to study two particular aspects of plastic deformation. The first is a study of the conditions which are necessary for unstable plastic deformation both at standard and elevated temperatures. The point in a test at which necks can develop in tensile specimens, their location, and the rate at which they will grow are being related to material and geometrical parameters. The second is a study of the growth and coalescence of voids, a ductile mode of failure, over a range of temperature that include both time dependent and time independent behavior. Of particular interest here is the influence of void interactions on unstable localized plastic flow and failure.

A third area of concern has been to develop a code capable of analyzing mass and thermal diffusion problems of a non linear and transient nature. Currently, this program is being used to study certain aspects of plastic flow due to mass diffusion. In particular, a study is being made of the influence of the interaction that exists between an edge dislocation and a vacancy on the climb rate of the dislocation as vacancies diffuse to or from the dislocation under the action of an externally applied stress. The dislocation climb rate and macroscopic strain rate are directly related.

(2) A Theoretical Study of High Temperature Failure Mechanisms

Graduate Student: G. M. Pharr

It has often been observed in practice that materials fail at high temperatures by the growth and coalescence of internal voids. It has also been noted experimentally that the rupture and deformation processes are related. We have been engaged in a theoretical study of this problem.

The basic approach has been to determine the growth behavior of holes in viscous media under uniaxial tension. The choice of a linearly viscous continuum allows us to solve certain of these problems analytically by applying a special simple case of the elastic-visco-elastic analogy to the elasticity solutions. Using this technique for single hole geometries has convinced us that a realistic model of ductile rupture must include the consideration of the interaction between holes.

In order to consider the effects of void interaction we have generated the solution for two circular holes in a plane viscous medium under axial tension applied normal to their common axis. This solution gives us information about the initial growth behavior of the holes as a function of applied stress and hole spacing. In addition, the complex variable technique employed allows us to follow the hole growth during shape changes analytically. It is expected that the model developed in this way will aid in understanding some of the problems related to high temperature creep failure.

(3) The Unloading Technique for Measuring Internal Back Stresses

Graduate Student: J. C. Gibeling, J. C. Wei

The measurements of internal back stresses which develop during high temperature deformation was first performed at Stanford several years ago. Since that time, this concept has gained fairly widespread acceptance and has even found some application in design considerations. During recent years, however, significant criticism and doubt has arisen regarding the validity of these measurements.

The most popular technique for measuring the back stresses which

act on dislocations in a deforming sample is the strain transient dip test. Here, a specimen undergoes creep until a steady-state rate is reached. At this point a portion of the load is removed, and the strain transient is observed. From the observed behavior, one can distinguish between two basic models of the dynamics of dislocation motion.

Our present work is aimed at maximizing the accuracy and sensitivity of this test in order to remove ambiguities which have previously existed in these observations. The three conditions which must be met are high strain resolution (1 microstrain), high time resolution (less than 0.1 seconds) and high unloading rates. To meet these requirements, our approach is to use resistance strain gages applied directly to the deforming sample, an oscillograph to record the output, and a nylon string which is burned to remove the load. Further, we are using lead specimens so that the deformation may conveniently be carried out at room temperature.

To date, this technique has been successfully applied to polycrystalline samples of lead. Analysis of the results indicates that they cannot be easily characterized in terms of a simple analytical model. Work is presently proceeding to apply the same technique to lead single crystals, so that the influence of grain boundaries can be eliminated.

#### (4) Investigation of the Processing Techniques of Dispersion Strengthened Metals

Graduate Student: P. S. Gilman, G. M. Pharr

Detailed studies of the high temperature deformation of dispersion strengthened metals have been made. However, in regards to the processing of these metals, studies have only produced certain empirical facts and the current processing methods are still largely guided by intuition. This research is directed at gaining an understanding of the mechanisms associated with the processing of these metals with the hope that a fundamental study of the mechanisms of processing

would help guide the manufacture and use of dispersion strengthened metals. Factors to be studied are grain boundary mobilities and crystallographic textures in these materials as well as the effects associated with the recrystallization of these materials.

The first and current stage of this investigation is a thorough search of published literature and industrial reports, augmented with direct industrial contact of the current state of knowledge concerning the processing of dispersion strengthened metals. With this knowledge we plan to simulate various processing techniques on model materials in order to investigate the various mechanisms of processing. One processing method to be explored is mechanical alloying which will utilize the Materials Science and Engineering Department's new attritor, high energy ball mill, to finely fragment the alloying elements used in the manufacture of dispersion strengthened metals.

Finally, the results of this research will give a much clearer picture of the important variables involved in the successful manufacture of dispersion strengthened metals.

(5) The Effects of Gas Bubbles and Voids on the Tension Creep Properties of Metals

Graduate Student: S. H. Goods

In an effort to further understand the structure dependence of high temperature deformation, we are examining the effects of inert gas bubbles and voids on the tension creep properties of silver. The embrittling mechanisms of a bubble or void microstructure are important as it is known that the mechanical properties of various fission reactor components degrade with time due to the formation of inert gas (He) bubbles.

Various procedures for introducing bubbles and voids have been investigated. The method chosen (because of its relative simplicity) involves the annealing of high purity silver in a variable oxygen atmosphere followed by a hydrogen anneal. In this way, water vapor

bubbles, chemically inert with the silver, are produced. The water vapor is found to nucleate both heterogeneously and homogeneously in silver, as does helium in structural metals within nuclear reactors. The bubble size and distribution is controlled by varying the partial pressures of the annealing atmospheres and annealing times.

The mechanical testing program has been recently initiated and the main emphasis here is to collect data on the untreated silver although tension creep tests on silver containing bubbles will begin shortly. It is hoped that a complete study of the effects of these bubbles on silver can be extended to further develop a general model for grain boundary cracking and brittle failure in metals in the presence of these microstructural defects.

(6) A Study of Creep of Dispersion Strengthened Single Crystals

Graduate Student: J. H. Holbrook

Research efforts have consisted of two aspects of the study of dispersion strengthened metals. One aspect consisted of testing dispersion strengthened single crystals in constant stress creep tests. Single crystal specimens were used in order to differentiate between strain contributions from a grain deformation and grain boundary sliding (gbs). These both occur in polycrystalline metals containing a dispersed, hard second phase. In some metal systems a large percentage of the creep strain comes from gbs, thus a stronger material could result by eliminating grain boundaries.

The metallic system selected for testing was a precipitation hardenable binary system of approximately one per cent silicon in aluminum. The precipitate is pure silicon, and because of its strength, stiffness, and incoherency it behaves much like a mechanical dispersoid. Creep tests of single crystals of aluminum with precipitates of silicon demonstrated strengths equivalent to those of polycrystalline Al-Si of equivalent volume fraction of silicon or better. Tests showed differences in creep stress dependence in high and low stress regimes. The transition stress is understood to be the

Orowan bowing stress for the material.

The second aspect of this research has involved an analytical examination of dislocation-dispersoid interaction. Topics considered were: effect of elastic mismatch between matrix and particle on stress dependence of climb-controlled creep; enhanced climb of edge dislocations when bent into a screw of configuration between particles; statistical effects of particle clustering upon dislocation glide; effects of stacking fault energy on mobile dislocation density; and creep contribution from diffusive movement of small dispersoids. These problems required extensive computer usage in simulating dislocation motion.

(7) High Temperature Creep of Ni-20Cr-2ThO<sub>2</sub> Single Crystals

Graduate Student: R. W. Lund

Single crystal tensile samples were cut from blocks of Ni-20Cr-2ThO<sub>2</sub> having large elongated grains. These samples were tested at various temperatures from 650°C to 1300°C and various stresses from 9500 psi to 55000 psi under constant stress vacuum creep conditions. Results of these tests have been beneficial in providing supportive evidence for two hypotheses which explain (a) heretofore anomalously high creep activation energies reported by many previous investigators for dispersion strengthened metals and (b) heretofore unexplained high stress dependence of dispersion strengthened metals.

We believe that the high creep activation energies result from neglecting the temperature dependence of the elastic modulus of the material. This modulus correction to the apparent creep activation energy is particularly important for materials having a high stress dependence (large stress exponent). Our calculations indicate that these anomalously high activation energies can be corrected to activation energies equal to those for self diffusion, as is the case for pure metals and many alloys.

We have also found that the high stress dependence of this material can be understood in terms of an asymptotic approach of the flow stress for the Ni-20Cr-2ThO<sub>2</sub> to the Orowan bowing stress. That is,

at a particular temperature and strain rate, the steady state flow stress in Ni-20Cr-2ThO<sub>2</sub> can be predicted by adding the steady state flow stress of Ni-20Cr to the calculated Orowan bowing stress of the Ni-20Cr-2ThO<sub>2</sub>. The predicted strain rate is found to agree within an order of magnitude with the strain rate determined experimentally.

We have also found that the very high temperature creep strength of this material is limited by diffusive coarsening of the ThO<sub>2</sub> particles. This limit is governed by the relationship between the kinetics of particles coarsening and the average interparticle spacing (which defines the Orowan stress).

#### (8) Creep of Fine Grained Materials

Graduate Student: J. R. Spingarn

We are studying the creep behavior of the fine grained materials at low stresses. Although the theoretical predictions of Nabarro and Coble are well known, direct experimental evidence is in short supply. We suspect that this regime may be crucial to understanding the role of grain boundary processes in sliding or superplastic materials. A second application we will explore is the effect of grain boundary density on mechanical properties when large defects such as radiation induced voids are introduced.

In order to obtain grain sizes in the range 1 - 10  $\mu\text{m}$  we are using high rate physical vapor deposition on high purity Al, Cu, and Ni, as well as codeposits of these metals with Al<sub>2</sub>O<sub>3</sub>. To utilize the large body of accumulated data on elastic modulus and self diffusion, we are concentrating on predominantly single element systems. As part of this study we are investigating the effect of processing variables such as temperature, composition, substrate chemistry and deposition rate on the microstructure of the deposits.

Early results indicate that the creep strength of vapor deposited materials is higher than conventional materials, while the ductility depends sensitively on the microstructure.



Reference Publications:

1. D. K. Matlock and W. D. Nix, "Effects of Helium on the High-Temperature Creep and Fracture Properties of Ni-6%W", Journal of Nuclear Materials, 56, 145 (1975).
2. R. W. Lund and W. D. Nix "On High Creep Activation Energies for Dispersion Strengthened Metals", Met. Trans., 6A, 1329 (1975).
3. W. D. Nix, "On the Possible Relation Between Grain Boundary Migration and the Kinetics of Grain Boundary Sliding in Polycrystals", Rate Processes in Plastic Deformation of Materials, ASM (1975).
4. M. A. Burke and W. D. Nix, "Plastic Instabilities in Tension Creep", Acta Metallurgica, 23, 793 (1975).
5. R. G. Stang, W. D. Nix, and C. R. Barrett, "The Influence of Subgrain Boundaries on the Rate Controlling Creep Processes in Fe-3 Pct Si", Metallurgical Transactions A, 6A, 2065, (1975).
6. R. J. DiMelfi and W. D. Nix, "Hole Growth in Plane Viscous Creep Including Interaction Effects", Int. J. Solids Structures, 12, 217, (1976).

#### 46. RECRYSTALLIZATION OF QUARTZ UNDER NON-HYDROSTATIC STRESS

A. M. Nur, Associate Professor, Geophysics

Graduate Student:

E. S. Sprunt

Agency Support:

Chevron Oilfield Research Company  
NSF (Graduate Fellowship)

Technical Objectives:

To understand the process of pressure solution in porous rocks. The program consists of two main parts: (1) a study of solution and redeposition of silica in an aggregate material -- sandstone, as a function of pore pressure and confining pressure, and (2) a study of the effect of stress on a single cavity in a rock.

Approach:

A jacketed hollow cylinder of the quartz aggregate is subjected to various combinations of pore and confining pressure at  $340^{\circ}\text{C}$  for about 250 hours. The samples are then carefully examined using a luminescope as well as standard petrographic techniques. The single pore is modeled by a circular hole drilled ultrasonically in a slab of novaculite-cryptocrystalline quartz. The slab is placed in a pressure vessel so that 150 bars of water pressure can be maintained at  $260^{\circ}\text{C}$  while the sample is subjected to a load perpendicular to the axis of the hole. The eccentricity of the hole is measured as a function of load and time.

Research Report:

A shaking-heating pressure vessel unit has been assembled for the hollow cylinder experiments. The system is operational, and experiments are currently in progress. An axial load vessel for the single cavity experiments has been designed and built. The problem

of sealing around the piston at 260°C has been solved. Further modification of the apparatus may be necessary, but preliminary experiments indicate that measurable changes in the eccentricity of the hole can be obtained in times of less than 100 hours.

Publication:

Sprunt, E., & A. Nur, "Porosity Reduction by Pressure Solution,"  
(in press) Geology, 1976.

## 47. TIME DEPENDENT CRUSTAL DEFORMATION

Amos Nur, Associate Professor, Geophysics

### Graduate Students:

G. M. Mavko  
S. C. Wang

### Agency Support:

NSF (Division of Earth Sciences)

### Technical Objectives:

Understand the nature of time dependent deformation processes in the earth's crust in relation to the prediction of very large earthquake, crustal breakup and the processes of mountain building in continental collisions.

### Approach:

Combine observational, laboratory and theoretical models to simulate time dependent deformation processes.

### Research Report:

#### (1) Postseismic viscoelastic rebound

The sudden appearance of a dislocation, representing an earthquake, in an elastic layer (the lithosphere) overriding a viscoelastic half space (the asthenosphere) is followed by time-dependent surface deformation, which is very similar to in situ postseismic deformation. The spectacular postseismic deformation following the large Nankaido earthquake of 1946 yields for the asthenosphere a viscosity of  $5 \times 10^{19}$  poise and a 50 percent relaxation of the shear modulus. Large thrust type earthquakes may provide, in the future, a new method for exploring the rheology of the earth's upper mantle.

#### (2) Melt squirt in the asthenosphere

The interpretation of the seismic low-velocity zone as a region of partially molten rock is extended to explain the transient displacements following the 1946 Nankaido earthquake. Three partial melt models are considered to account for the observed time constant

of 3-5 years: large-scale diffusion of melt through a porous matrix can decay over thousands to billions of years and is much too slow. Simple shearing in 'penny-shaped' cracks happens on a seismic time scale and is much too rapid. Interconnected penny-shaped cracks at different orientations with respect to the principal stresses respond on an intermediate time scale by short-range melt squirt from one crack to another, providing a reasonable mechanism to account for the transient deformation at Nankaido, while components of shear parallel to each individual crack relax quickly according to the better-known mechanism for seismic attenuation in the low-velocity zone.

### (3) Slip rates and morphology of continental collision belts

The widths of the Iran and Tibet collision segments of the Alpine belt are proportional to the local collision rates. Both segments are plateaus, but stand at different elevations. The simplest explanation for the width-rate correlation is that both increase with distance from the pole of relative rotation of the colliding plates. The difference in plateau height can be explained by the conservation of total mass flow into the collision belt. The width slip rate relation provides a tool for estimating ancient plate motions. For example, the inferred Uralide collision rate was 5-9 cm/y, with an associated pole of rotation at 81°N 75°E.

#### Publications:

- Nur, A. & G. Mavko, Postseismic viscoelastic rebound, *Science*, 183, 204-206, 1974.
- Mavko, G. & A. Nur, Melt squirt in the asthenosphere, *J. Geophys. Res.*, 88, 1444-1448, 1975.
- Ben-Avraham, Z. & A. Nur, Slip rates and morphology of continental collision belts, *subm. to Geology*, 1976.

#### 48. VELOCITY AND ATTENUATION OF SEISMIC WAVES IN ROCKS

A. M. Nur, Associate Professor, Geophysics

Post Doctorate:

Hisao Ito, Japan Geological Survey

Graduate Students:

R. P. Denlinger  
M. A. Grosenbaugh  
J. D. Weeks

Agency Support:

NASA (Lunar analysis program)  
USGS (Geothermal program)  
NSF (Div. of Earth Sciences)

Technical Objective:

(a) To understand the physical processes which control the propagation, reflection, dispersion and attenuation of seismic waves in porous rocks with fluids. (b) Apply the results to earthquake prediction, geothermal exploration, oil resources and lunar and terrestrial crusts.

Approach:

Experimental study of wave propagation in the laboratory at high temperature, confining pressure and pore pressure, using the pulse transmission method.

Theoretical study of velocity and attenuation models of the earth's and the lunar crusts, geothermal fields with transition from hot water to steam, and dilatant rock behavior.

Research Report:

(1) High pressure, pore pressure and temperature

Compressional and shear wave velocities have been measured in Westerly granite under conditions of high temperature to 500°C, high confining pressure to 5 kbar, and independently controlled pore water pressure. Measurements in a dry sample show that at a given temperature, confining pressure has a larger accelerating effect on com-

compressional wave velocity ( $V_p$ ) while at a given confining pressure, temperature has a larger retarding effect on shear wave velocity ( $V_s$ ). The combined effects of temperature and pressure act to increase Poisson's ratio in a dry rock. Increasing the temperature of a sample that contains pore water at low pressure causes a continuous decrease in the bulk modulus ( $k$ ) and  $V_p$ , while the shear modulus ( $\mu$ ) and  $V_s$  are affected only by the temperature of the crystalline matrix. The low  $V_p$  and nearly unchanged  $V_s$  cause a decrease in Poisson's ratio. Under otherwise identical conditions of pressure and temperature, high pore fluid pressure causes a decrease in  $\mu$  and  $V_s$ , while  $V_p$  is less affected, and Poisson's ratio increases. This trend continues until at high temperatures the bulk modulus of the pore water decreases and results in a decrease in  $V_p$ . Gassmann's theory is found to predict closely the compressional and shear wave velocities of saturated porous samples from the elasticity of their dry crystalline matrix and the known properties of water. Finally, time-dependent compressional velocities may be caused in laboratory samples by solution of quartz in supercritical pore water.

## (2) Velocity in the lunar crust

The top 25 km of the lunar crust are characterized by a very large increase of velocity with depth, followed by almost constant velocity below 25 km, presumably due to lack of cracks. Because of extensive meteoritic impacts we expect extensive fracturing of the lunar crust to depths comparable to the dimension of impact craters, some of which are hundreds of kilometers in diameter. The increase with depth of  $V_p$  near the lunar surface is too great for gravitational self-compaction of fractured rock, as shown by Warren et al. (1972) and Talwani et al. (1973). It is also extremely unlikely that the velocity gradient is controlled in this region by mineralogy. Instead, it must be controlled by the systematic decrease with depth of the average crack density. Alternatively, it is possible that the large change is confined to the first 1-2 km, (Kovach et al., 1973) and the velocity at greater depth is almost 'normal' for self-compacting fractured rocks.

in any case, laboratory data combined with in situ travel time data must be used to provide some constraints on the mechanical state of the shallow crust.

We have made a detailed study of velocities as a function of pressure and temperature history although without vacuum, in simulated lunar material - a fine grained volcanic ash. The results yield relations between compressional velocity and density vs. the temperature and pressure histories. The duration of pressure and temperature cycles lasted on the order of days to weeks, and the results are assumed to represent equilibrium values for durations of that order. In general, rapid changes occur in the initially loose sample to transform it into a more and more competent rock-like solid. In particular, moderate temperature causes very rapid permanent compaction. Both temperature and pressure act to compact the rock powder, but the rate of compaction with heating to a given temperature is greater at low pressure. Thus the velocity of ash at constant  $P = 50$  bars and room temperature, has increased from 2.3 km/sec to 3.0 km/sec, 3.3 km/sec, and 3.5 km/sec after heating cycles to 130°C, 180°C and 220°C respectively. At constant  $P = 2.5$  kbr, velocity increases from 3.8 km/sec to 4.4 km/sec after heating to 220°C. The measured velocity density relations for permanently compacted ash show that the effect of heating is to increase velocity much more than density, indicating that fast processes occur at grain boundaries to solidify the powdered rock.

The permanent increase of velocity is, to a first approximation, simply related to the maximum temperature, and not the temperature history which preceeded the maximum. In other words, the physical state of the sample is determined only by the highest pressure and temperature which it experienced, provided it achieved, under these conditions, equilibrium.

In summary we have found that rock powders which remain unchanged following long periods of cold compaction, rapidly undergo permanent increases of their elastic stiffness even at moderate temperatures.



Publications:

- Spencer, J.W., and Amos Nur, The effects of pressure temperature and pore water on velocities in Westerly granite, J. Geophys. Res., 81, 899-904 (1976).
- Nur, A., N. Fujii, & E.S. Sprunt, Velocity structure of the shallow moon, Abst., 7th Lunar Science Conf., 633-636 (1976)

#### 49. MECHANICAL PROCESSES OF CRUSTAL FAULTING

Amos Nur, Associate Professor, Geophysics

David M. Barnett, Associate Professor, Materials Science

Professional Associate:

B. Freund, Brown University

Graduate Students:

K. D. Mahrer

M. L. Bell

Agency Support:

USGS (Earthquake Prediction Program)

Technical Objectives:

Study faulting and related nonlinear deformation processes from a standpoint of fracture and continuum mechanics.

Approach:

Faulting models based on uniform stress, friction and slip fail to explain major observed features of crustal faulting, e.g., frequency-magnitude relations, seismic and aseismic slip, and precursory tilt events. In our present work we combine available field deformation data with recent experimental laboratory results on the deformation of rocks under crustal conditions to study realistic mechanical processes of seismic and aseismic crustal failure. The investigation of these processes utilizes recent developments in fracture and dislocation theories, including time-dependent and spatially variable fault slip.

Research Report:

To date we have completed: (1) the theoretical work on surface deformation due to fault slip with finite stress for antiplane and plane elastic models; (2) developed 3 levels of models for rupture of lithosphere associated with time dependent slip and creep; (3) made significant progress in determining the role of spatially variable stress in faulting; (4) developed a simple point model and a simple continuum model for dilatancy.

Publications:

Freund, L.B., & D.M. Barnett, A two dimensional analysis of surface deformation due to dip slip faulting, Bull. Seism. Soc. Am., in press, 1976.

Nur, Amos, A note on the constitutive law for dilatancy, Pageophy., v. 113, 197-206, 1975.

Barnett, D.M. & B. Freund, An estimate of strike slip fault friction stress, Bull. Seism. Soc. Am., in press, 1976.

Bell, M. Lee, M. Zoback, and A. Nur, A micromechanical model for dilatancy, subm. for publ., J. Geophys. Res., 1976

50. PHOTON PRODUCTION FROM HIGH ENERGY ELECTRON BEAMS

R. H. Pantell, Professor, Electrical Engineering

Professional Associates:

M. A. Piestrup

G. B. Rothbart

Graduate Students:

C. K. Chen

A. N. Chu

H. Park

Y. Park

Agency Support:

NASA NGS-7110

ERDA EO4-3-326-PA42

NSF - ENG-71-02378-A01

Technical Objectives:

(1) To obtain sources of vacuum ultraviolet, x-ray, and  $\gamma$ -ray emission for materials research.

(2) Develop an optical klystron.

Approaches:

(1) Develop a Cerenkov light source that provides a continuum of radiation from visible wavelengths to  $600\text{\AA}$  and to use this emission for various spectroscopic studies.

(2) Investigate electromagnetic radiation from channeled electrons with the possibility of developing a light source for the x-ray and  $\gamma$ -ray region that has 5-10% bandwidths, that is tunable, and that is several orders of magnitude more intense than the brehmsstrahlung background.

(3) Develop tunable, optical amplifiers, oscillators and harmonic generators based on the principle of the klystron.

Research Report:

(1) Vacuum Ultraviolet Emission from Cerenkov Radiation

Spectral power density from Cerenkov radiation was measured in the vacuum ultraviolet from 2000 to 620Å. The radiation was produced by passing a 500 MeV, 1 ma peak current electron beam through 1.4 meters of one atmosphere of helium gas at room temperature. In the photon energy range from 6 to 20 eV, approximately  $10^{14}$  photons per second per Angstrom per milliamperere of electron beam current were emitted. The upper photon energy limit at  $\approx 20$  eV is determined by the 584Å resonance in helium.

Although the theory of Cerenkov radiation was developed almost forty years ago, our measurements are the first direction confirmation of the theoretical power spectrum of Cerenkov radiation in the vacuum ultraviolet. Theoretical calculations show the photon production of V.U.V. to be better than synchrotron emission by 3 to 4 orders of magnitude.

A larger mirror is being designed to utilize the entire Cerenkov cone. This mirror will use the 20 GeV electron beam at Stanford's Linear Accelerator Center to produce the V.U.V. emission.

Reference Publication:

1. M. A. Piestrup, R. W. Powell, G. B. Rothbart, C. K. Chen and R. H. Pantell, "Cerenkov Radiation as a Light Source for the 2000 to 620Å Spectral Range", Appl. Phys. Letts. 28 (1976).

(2) X-ray and  $\gamma$ -ray Emission from Channeled Electrons

A theoretical analysis of the radiation characteristics associated with the periodic trajectories of a channel electron inside a crystal has been done. The analysis shows that the photon energy resolution can be quite good, on the order of several per cent, with an intensity per unit length for an electron that is several orders of magnitude greater than brehmsstrahlung. The emission wavelength may be tuned by altering the electron energy. There are few narrow band sources of radiation in the KeV to MeV range, and more that are tunable and of high intensity. KeV photons may be used to investigate inner shell

absorptions in higher Z-number atoms, and MeV photons are useful for studying photonuclear cross sections.

### (3) An Optical Klystron

We have measured momentum modulation of a 100 MeV electron beam by a 1 M.W. Nd:YAG laser. We are now constructing a Dye laser and 6 MeV electron beam source to achieve similar modulation and bunching of the electrons. Theoretical analysis of the optical klystron and a Monte Carlo computer simulation have been performed to demonstrate the possibility of optical bunching and klystron operation.

## 51. PHYSICS AND CHEMISTRY OF OXIDES AND OXIDE SURFACES

G.A. Parks, Professor, Applied Earth Sciences

### Graduate Students:

R. L. Bassett  
R. P. Ebro  
J. P. Murray  
R. M. Railey\*  
L. J. McAllister

\*Received Ph.D. during report period

### Agency Support:

U. S. Geological Survey

### Adsorption of Aqueous Solutes onto Solids

Several adsorption isotherms with differing theoretical origins are available in the literature (e.g. James et.al. 1975). All account well for the pH dependence of the adsorption densities of several metal ions and their hydrolysis products onto simple oxides. They permit a considerable degree of prediction and are able to account for inorganic complexation of the adsorbate but do not account for variability of the solid phase. Among all solids which have been studied as adsorption hosts for heavy metals, most are characterized by a single type of behavior. The simple ideal oxides such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  typify this behavior (MacNaughton and James, 1974). Two solids of great importance in natural and industrial systems, montmorillonite and the  $\text{MnO}_x$  oxides behave differently (MacNaughton, 1973). None of the adsorption isotherms available adequately describes adsorption onto these solids. None of the models has been tested or adapted to describe adsorption of anionic species such as  $\text{F}^-$  or  $\text{H}_3\text{BO}_4^-$ .

### Technical Objective:

1. Criticism and analysis of existing ion exchange and adsorption models from the points of view of capability and compatability with aquatic chemistry and/or hydrologic models.

2. Appraisal of the problem of dealing with simultaneous adsorption by many solids present in a single aqueous system. Define means of characterizing solids as adsorbents.
3. Appraisal of the problem of simultaneous adsorption of several solutes present in a single system onto one solid adsorbent.
4. Appraise published information on montmorillonite and manganese dioxides in search of reasons for the differences in behavior of these materials from the simple solid oxides.
5. Experimentally obtain adsorption data in system selected to contribute to objectives 1-4 and to meet environmental or technological need.

Approach:

We are working toward these objectives on several fronts, with emphasis dictated by availability of funding. During the year just past we have had only indirect funding for any project, thus progress has been slow. However we expect a grant from the U.S. Geological Survey in support of these specific objectives and anticipate participation in an interdisciplinary E.P.A. project which will permit some progress.

Analyzing Isotherms: Adsorption of Boron from Aqueous Solution onto Oxides and Silicates (Bassett). In a project supported entirely by the U.S. Geological Survey and performed in their laboratories, we are studying adsorption of boron from water onto oxide and silicate minerals, including clays; this problem is of practical importance because the boron content of wastewaters produced during geothermal power production in California is sufficiently high that it is toxic to many crop plants.

There has been a great deal of work done on this subject by others. Most published work, however is so limited in the scope of variables that realistic testing of adsorption models is precluded. We have identified areas of scarcity in the matrix of variables and systems of



available data and are collecting experimental data in these areas.

Results to date indicate that, if solution chemistry is adequately accounted for, existing adsorption isotherms will probably prove adequate to describe the behavior of boron.

Competitive Ion Exchange Adsorption of Cations (McAllister).

We are studying competitive adsorption of  $H^+$ ,  $Ca^{++}$ , and  $Cu^{++}$  on  $\alpha FeOOH$  (Goethite). Experimental difficulties have been overcome and measurements are in progress, but we have no substantive progress to report.

Adsorption of Organic Constituents of Water (Murray). The

transmission of viral diseases, such as infectious hepatitis and viral gastroenteritis, is a serious problem in reuse of polluted water. From study of complex formation between aqueous metal ions and proteins and amino acids and sparse published data we are lead to believe that adsorption of viruses to mineral surfaces could involve sufficient energy to disrupt and inactivate the virus. The adsorption energy should be strongly dependent upon the cation in the solid and the bulk and surface properties, such as perhaps polarizability, of the solid. We expect that verification of this hypothesis will lead to the ability to design sand filters capable of irreversibly removing viruses from water and predicting the ability of soils to remove viruses from water reinjected into the ground.

The research is based upon measurements of the adsorption densities of virus particles onto selected solids ( $SiO_2$ ,  $MnO_2$ ,  $Fe_2O_3$ ,  $CuO$ ) and determination of the infectivity and composition of desorbed material. Results to date show that  $MnO_2$  is many times more effective in removal of viruses from water than is  $SiO_2$ .

Impact of Research. Our work over the past few years, particularly that with adsorption of  $Hg(II)$  onto  $\alpha FeOOH$  by Avotins, has attracted considerable interest among hydrologists and environmental groups concerned with water pollutant transport and pollution abatement.

Assessment, management, and protection of water resources depends in part on our ability to forecast, interpret, and quantitatively model the release, dispersion, and fixation of solutes which affect water quality. Lack of critical analyses of ion exchange and adsorption models for this application, lack of data, and difficulty in characterizing naturally occurring solids as adsorption hosts constitute a bottleneck in attaining water quality modelling capability required for decision making. The U.S. Geological Survey, recognizing this, has committed funds for the 1976/77 academic year to enable our group to focus to a larger extent on these problems.

Reference Publications:

1. James, R.O., P.J. Stiglich, and T.W. Healy (1975) Analyzing Models of Adsorption of Metal Ions at Oxide/Water Interfaces, Faraday Discussions of the Chemical Society, No. 59, p. 142-156.
2. MacNaughton, M.G. (1973) Ph.D. Dissertation, Department of Civil Engineering, Stanford University.

52. GAS-LIQUID METAL REACTIONS AND INTERACTIONS. PRODUCTION OF REACTIVE METALS VIA CARBOTHERMIC REDUCTION IN SOLVENT METALS. SPENT NUCLEAR FUEL RECOVERY. NUCLEAR WASTE UTILIZATION AND DISPOSAL.

Norman A. Parlee, Professor of Extractive Metallurgy

Active Advisors and Collaborators:

Prof. R. N. Anderson  
Prof. Hans C. Andersen

Graduate Students:

K. W. Au\*\*  
E. V. Auza\*  
N. Bakshani  
J. H. Hou  
A. Jayarajan  
G. S. Selvaduray  
J. R. Hwang  
Z. Tekneci  
S. Savcioglu

\*\*Received M.S. during report period  
\*Received Ph.D. during report period

Agency Support:

NSF DMR 75-08168  
ERDA AT(04-3)326,P.A. #28  
NSF/MRL through CMR  
Argonne National Laboratory (ERDA)

Technical Objective:

1) To study the solubilities and rates of diffusion of gases (e.g.  $H_2$ ,  $N_2$ ,  $O_2$ ) in liquid metals and alloys and thus to predict or calculate rates of removal of gases from liquid metals and alloys, or introduction of gases into liquid metals and alloys, 2) To find cheaper ways of making expensive reactive metals (e.g. Ti, U, Zr, Mg), 3) To develop a better method of recovering unburned poisoned nuclear reactor fuel, 4) To develop better ways of utilization and disposal of nuclear reactor wastes.

Approach:

Determination of the thermodynamics and kinetic relations from equilibrated and dynamic systems in the laboratory. Development of methods of prediction and/or calculation of the behavior in real

industrial systems.

Research Report:

(1) The Absorption, Evolution and Diffusion of Gases in Liquid Metals

Graduate Students: E. Auza, A. Jayarajan and J.H. Hou

The gases (hydrogen, nitrogen and oxygen) in most cases must be removed from the liquid metals before they are cast if optimum final solid properties are to be achieved (nitrogen is sometimes an exception where it is added in high alloyed important austenitic steels to save expensive nickel). Rates of gas removal are basically controlled (in liquid vacuum degasification or argon flushing etc.) by gas diffusivities - in the absence of excessive amounts of a surface active element, (e.g. O), which is generally previously removed. Thus knowledge of diffusivities in liquid metals and alloys is important.

This laboratory has carried out many studies of solubilities, rates of absorption and effusion in stirred and stagnant melts, and measured diffusivities of H, N, O, in a considerable number of gas-metal and gas-alloy systems. Diffusivities have been measured by "unsteady state" and "steady state" methods developed here, which give identical results on the same clean system. Sacris and Parlee showed that there appeared to be a linear relationship between  $\log D_H$  and hydrogen solubility in metals. Depuyt and Parlee showed that there were linear relationships in Fe-X binary alloys between (a)  $\log D_H$  and interaction parameters ( $e_H^X$ ) and (b)  $\log D_H$  and hydrogen solubility, for the 1st and 2nd long periods in the periodic table. Lee and Parlee showed analogous relationships existed for  $D_N$  in Fe-X alloys and that relation (b) was particularly useful (and easy) in prediction of  $D_N$ , and not as sensitive to periodic table position of alloying element.

Auza's recently completed Stanford Ph.D. dissertation (a) shows that the predictive linear relationships for  $D_N$  (found by Lee and Parlee) can be extended to complex iron alloys and steels of Fe-U-V-W-X-Y-Z compositions up to 10% of total alloying element and

looks favorable for 20% and above, and (b) developed a completely new and spectacular graphical method of predicting  $D_N$  in alloys of Fe-U-V-W-X-Y-Z composition or any steel up to 10% total alloying elements regardless of periodic table position. This method is based on known curves of  $\log D_N$  vs Fe-X, and theoretically based on a Taylor Series Expansion which appears to make it possible to predict  $D_N$  in all steels up to very high alloy contents, say, 50% total alloying element, which are so important in special steels, and in special processes including plasma-arc processes, electron beam melting etc.

The present research is engaged in two directions (a) Extension of Auza and Parlee's measurements and predictive methods to these very high complex alloys (~50%) so important in many applications - and where nickel can be saved, and adaptable to plasma arc preparation. (b) Checking and rechecking the limits of the effects of surface active elements O, S etc. on nitrogen absorption and gas removal by vacuum. It is expected the present research will make it possible to predict  $D_N$  in any complex iron alloy or steel, not excessively high in O and S, and make degasification and gas control in iron alloys and steels completely predictable. (Hydrogen offers a less serious problem because it diffuses so rapidly and is removed so fast by vacuum degasification). Perhaps it should be mentioned that by using our unsteady and steady-state methods combined, we were able to measure the effect of C on nitrogen solubility in liquid iron and resolve an international controversy.

This research is all part of a U.S.-U.S.S.R. co-operative project on the commercial development of plasma-arc processes.

## (2) The Calculation of Diffusivities, Viscosities etc. for Liquid Metals and Alloys from Atomic Properties

Graduate student: Z. Tekneci

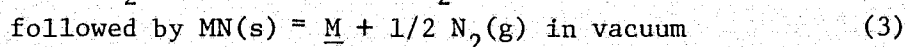
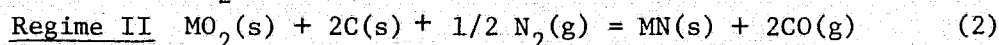
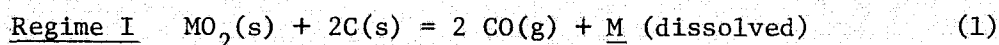
Millions of dollars can be saved if such transport properties can be calculated rather than measured in the laboratory. Up until our recent work at Stanford none of the proposed theories and methods

has been generally successful, and particularly in the case of diffusivities of gases in metals. The now Dr. Protopapas, with Profs. Andersen and Parlee, started with the Enskog Theory, modified it, corrected it, used hundreds of computer calculations to develop reliable constants, temperature coefficients and corrections, to achieve a theory and general method which, for nearly all liquid systems, makes it possible to calculate from atomic properties (1) Self Diffusivities (2) Viscosities in Pure Metals and Binary Alloys and (3) Diffusivities of Gases (H, N, O) in Metals. It is believed that these methods can be extended to all complex liquid alloys. Mr. Tekneci is now engaged in the problem of extending the calculation of Gas Diffusivities to Complex Alloys including all low and very highly alloyed steels where the results would be of tremendous importance.

(3) Production of Expensive Reactive Metals (e.g. U, Ti, Zr, Mg) via Carbothermic and Carbonitrothermic Reduction of Their Oxides etc. in Liquid Solvent Metals

Graduate Student: N. Bakshani

A paper has recently been published describing many preliminary experiments which have shown that most expensive reactive metals can be produced by the cheap reducing agent carbon instead of by the conventional expensive reducing agents (such as Mg) or by fused salt electrolysis which used the most expensive form of reduction energy - electricity. Conventional carbothermic reduction either results in complete carbide formation or serious carbide contamination, both of which are avoided by the proposed method. Also the solvent reduction method involves much lower temperatures and thus serious container problems are avoided, also energy requirements are lower. Two different reduction regimes have been used, as below, where M represents the reactive metal dissolved in the liquid solvent



(Reaction 2 is thermodynamically extremely favorable (low  $\Delta G^\circ$ ), goes well). The reactive metal can be recovered from the solvent by one of several methods, such as evaporation or distillation, phase separation, metallic or other extraction, precipitation methods etc.

Present and future work is aimed at determining the best and most economic ways to produce these metals in marketable state and purity. Due to insufficiency of funds one metal had to be chosen for truly definitive work to study and really prove the process, with small attention to certain other metals. Uranium was chosen because (a) it is a typical reactive metal, (b) the solvent reduction of partially spent  $UO_2$  reactor fuel is one step in our nuclear fuel reprocessing method (described later), (c) we have much experience with U systems and much sound activity data of U-Sn etc. liquid solutions, needed to make our research quantitative and definitive. Thus uranium was chosen as a "pattern" or "prototype" metal rather than (say) Ti or Zr which may be more important commercially.

Mr. Bakshani's Ph.D. work on uranium is nearly complete. Due to the time factor and its comparative simplicity he has concentrated on Regime I, and recovery of the metal. His accomplishments to date are as follows: (1) he has established that reaction  $UO_2(s) + 2 C(s) = 2CO(g) + U$  is the overall reaction in Sn solvent and that carbides are not produced in the liquid alloy because Sn lowers  $a_U$  to the point where  $U_xC_y$  cannot form, (2) the effective equilibrium constants of the reaction in the range of 1200-1650°C, (3) the reaction goes well and reasonably rapidly at 1450-1500°C at moderately reduced pressures, e.g. <0.3 atm. with no problems, in his induction heated crucible, (4) the degree of completion is around 99% and would be close to 100% in larger industrial sizes, (5) separation of U from the Sn solvent (other solvents are possible but Sn is a good one) can be achieved by evaporating the Sn by induction or electron beam or by the Mg separation method, (6) Ti, Si, Zr and Mg can definitely be reduced by Rx.1 Regime I - and that probably commercial electronic grade Si can be produced and easily separated, (7) Uranium and Titanium can definitely be reduced into the solvent by Regime II.

Both (6) and (7) are a continuation of previous preliminary work, requiring definitive future research.

Bakshani needs yet to check the degree of purity of the U produced (only roughly checked in preliminary work), to recheck his separation methods and look at one or two others, and to consider methods of increasing purity if not satisfactory (there are several methods).

It is hoped that Bakshani's work on uranium production will serve as a guide for future research leading to less expensive critical reactive metals.

(4) The Recovery of Spent or "Unburned" Nuclear Fuel - Consisting of Normally 95+ % Re-useable Fuel

Graduate Students: K. Au, S. Savcioglu

A subject not known to the lay public is (1) that uranium nuclear fuel is only "burned" to an extent between 95 and 99% in power reactors before the fuel "rods" are poisoned, and must be replaced by new fuel "rods" (really tubes) and (2) that the first multi-million dollar plant for recovery of the "unburned" fuel for reuse (by a years long process involving environment contamination problems) has been reported by the scientific and commercial press as inoperable. The <95% unburned fuel from the many nuclear power plants is simply being stored as ever increasing inventory. Obviously until a workable process and plant for reprocessing, i.e. recovery of the >95% unused fuel, is devised one cannot expect nuclear power to achieve its great economic potential, its optimum safety and proper conservation of limited uranium ore reserves. Professors Anderson and Parlee over a more than 3 year research have, with their graduate students (the now Drs. Schicks, Fuwa, and others) developed on the laboratory scale the definitive basic science of a new and promisingly workable process for this reprocessing-recovery. This fully documented basic process depends on the selective nitride precipitation and separation of purified uranium and plutonium, leaving behind in solution the fission products which originally poisoned the fuel rods, and made necessary their removal from the reactors. At present the spent fuel is simply stored at immense inventory cost, pending the development of a



successful method of re-processing.

Our proposed process involves the dissolution of the spent fuel in a liquid metallic solvent (of special properties) such as tin, the nitriding of the uranium (or plutonium) by the typical reaction  $\text{U (dissolved)} + 1/2 \text{N}_2(\text{g}) = \text{UN(s)}$  to form a precipitate which sinks to the bottom of the vessel, leaving the waste fission products dissolved in the supernatant tin (or other suitable solvent). Thus the purified UN can be separated from the fission product poisons, re-used as a new fuel itself, or reconverted to U fuel by vacuum denitrification or phase separation methods, or reconverted to  $\text{UO}_2$  fuel by oxidation in the liquid system. All can be achieved at temperatures and pressures easily workable in modern induction furnace technology. Much easier and safer disposal of radioactive wastes appears possible. There does not seem to be any reason why the process cannot be developed to commercial size, if funds are made available. Dr. Fuwa demonstrated in his Ph.D. thesis here (1974) that the separation could be performed on simulated spent nuclear fuels and that recovery of at least 90% re-usable fuel should be possible.

The most recent work here has been by Mr. Kenneth Au who investigated several solvent metals other than tin. More work needs to be done but one rather spectacular discovery was made, namely that Sn-Ni solvents of the proper composition cause the UN(s) to precipitate to the bottom in a coherent mass unwetted by the solvent thus making the UN separation clean cut and thus not involving certain engineering methods of separation which might otherwise be a more expensive step in the actual overall process. Solvent metals are expected to be recycled and reused.

Proposed future work involves looking at cheaper or better solvent metals, also assessing the best of several methods of recovering the purified fuel from the solvent in the most desired form, which some years ago was U, now is  $\text{UO}_2$ , but may be UN in the future. Mr. Savcioglu has begun preliminary work on the precipitation of uranium hydride from low melting solvents. The selective hydride separator might turn out to be superior to the nitride method, also it offers

another possible route for separating very reactive metals from the solvent after carbothermic reduction of reactive metal oxides in solvent, described under project (3) above. Hydrides can be much more easily (at lower temperatures) decomposed to the metal than the nitrides.

#### (5) Nuclear Waste Utilization and Disposal

Graduate Students: G.S. Selvaduray and J.R. Hwang

In modern conventional power reactors the spent fuel rods (or tubes) contain mainly two kinds of wastes (1) the radioactive fission products mixed with the unburned fuel, and (2) the contaminated zirconium alloy "hulls" or cladding after the spent fuel is removed from the now and somewhat altered cladding tubes.

The separation of the wastes from the  $\text{UO}_2$  fuel itself has been dealt with under project (4) above, where it is found that these radioactive wastes can be concentrated into a metallic block matrix of Sn or other corrosion resistant metal which (a) reduces emanation (b) is easy to handle and dispose of, and (c) is highly unleachable to ground waters.

The zirconium "hulls" are a problem because (a) they are contaminated and (b) zirconium is very expensive and should be recovered if possible. This laboratory is carrying out an assessment of the zirconium problem, using first the selective ZrN precipitation in liquid Sn (and other solvents). Short lengths of Zr hulls have been dissolved in liquid tin, nitrified with  $\text{N}_2$  gas to precipitate the ZrN to the top, leaving the fission product contaminants behind in the liquid solution below. On solidification the radioactive fission product fraction remains locked up in an easily disposable essentially unleachable matrix. So far the research suggests a favorable process can be developed. Next steps are (a) definition of best conditions for ZrN precipitation, including best solvent (b) recovery of Zr from ZrN, which appears possible by several methods (c) greater concentration of the wastes in the metal block-several methods are possible (d) taking a look at the quite stable zirconium hydride as either the means of precipitation-separation from the contaminants or the easiest route to final recovery of the zirconium (since ZrH is far easier to decompose

by vacuum than is ZrN).

Publications:

1. Edwin Auza. Stanford Ph.D. dissertation, "The Diffusion of Nitrogen in Liquid Iron Alloys at 1600°C", June 1976.
2. P. Protopapas, H.C. Andersen and N.A.D. Parlee, "Theory of Transport in Liquid Metals. II. Calculations of Shear Viscosity Coefficients", Chemical Physics, 8. (1975) 17-26.
3. P. Protopapas and N.A.D. Parlee, "Theory of Transport in Liquid Metals. III. Calculation of Shear Viscosity Coefficients of Binary Alloys", Chemical Physics, 11, (1975), 201-215.
4. P. Protopapas and N.A.D. Parlee, "On a Theory for the Derivation of a Single Hard-Sphere Potential Describing the Overall Molecular Interactions in Binary Liquid Metal Alloys as a Function of Temperature and Composition", J. High Temp. Sci., 7, (1975) 259-287.
5. P. Protopapas and N.A.D. Parlee, "Theory of Transport in Liquid Metals. IV. Calculation of Inter-diffusion Coefficients of Gases in Metals", submitted 1976 to J. High Temp. Science.
6. A. Fuwa, R.N. Anderson and N.A.D. Parlee, "Thermodynamics of Nitride Formation in Liquid U-Gd-Sn Alloys". J. High Temp. Science 7, 249-258 (1975).
7. R.N. Anderson and N.A.D. Parlee, "Carbothermic Reduction of Refractory Metals". J. of Vacuum Science and Technology, vol. 13, No. 1, Jan/Feb. 1976.
8. Kenneth Au, M.S. Report, Dept. of Applied Earth Sciences, Stanford University, Nov. 1975, "The Thermodynamics of Nitride Formation Reactions in Molten Uranium-Tin-Nickel Alloys".

53. ELECTRICAL, OPTICAL AND METALLURGICAL PROPERTIES OF SEMICONDUCTING MATERIAL

G. L. Pearson, Professor, Electrical Engineering

Professional Associates:

B. L. Mattes  
C. Yeh

Graduate Students:

K. I. Chang  
K. Y. Cheng\*  
Y. M. Houng  
K. G. Jew  
J. S. Kim  
C. C. Shen  
Y. D. Shen

\*Received Ph.D. during report period.

Agency Support:

Navy N00014-67-A-0112-0044  
AROD DAHC04-75-0013  
NSF GH-34549  
Rockwell International F-19628-74-C-0038  
NASA NSG-1201  
JPL 954245

Technical Objective:

To prepare new semiconducting materials, measure their pertinent properties, and construct novel devices therefrom.

Research Report:

(1) Preparation and Properties of  $\text{Al}_{1-x}\text{Ga}_x\text{Sb}$

Graduate Student: K. Y. Cheng

The ternary phase diagram of the Al-Ga-Sb system was established in the Ga-rich region. The weight loss technique was used to determine the liquidus data at 400, 450, 500 and 550°C. Solidus data were measured by means of electron beam microprobe analysis on epitaxial layers grown from the Al-Ga-Sb melt near 500 and 550°C. Under the assumptions

that the binary liquid systems are simple solutions and that the ternary solid forms an ideal solution, excellent agreement was obtained between the calculated liquidus and solidus isotherms and experiment.

$\text{Al}_x\text{Ga}_{1-x}\text{Sb}$  layers with Al concentration  $x$  varying from 0.0 to 0.92 were grown on (111) oriented GaSb substrates in a Ga-rich melt using a vertical dipping liquid phase epitaxy system. Growth criteria which control the crystal composition during growth and yield high quality single crystals were determined. The physical properties of the epitaxial crystal layers were also examined.

The dependence of bandgap energy on Al concentration  $x$  in the mixed crystal was measured in undoped layers using optical absorption, wavelength modulated absorption, photoluminescence and electron beam microprobe techniques at 77 and 300°K. The variations of the bandgap energy with Al composition  $x$  in the (000), (100) and (111) directions are all quadratic with positive bowing parameters. Double crossover points along the conduction band minimum were observed.

The infrared lattice vibration spectra of the  $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$  system were studied in the reststrahlen region. Room temperature reflectance spectra were measured in a double beam mode at near normal incidence in the spectral range from 180 to 520  $\text{cm}^{-1}$ . Two-mode behavior was observed over the entire composition range investigated, i.e.,  $x = 0.05$  to 0.92. Oscillator parameters were obtained by a fitting procedure in which the experimental reflectance was compared with a reflectance synthesized from damped harmonic oscillators. The composition dispersion in the TO phonon branches was studied by using the random element isodisplacement (REI) model. The six-parameter REI model was found to be the best approach in describing the  $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$  system.

## (2) Grown Junction GaAs Solar Cells

Graduate Student: C. C. Shen

In this work,  $p(\text{Al}_x\text{Ga}_{1-x}\text{As})-p(\text{GaAs})-n^+(\text{GaAs})$  solar cells with grown p-n junctions are fabricated and investigated. Minority-carrier diffusion lengths in Ge-doped liquid phase epitaxial (LPE) GaAs layers are evaluated by using scanning electron microscope (SEM) beam-induced current techniques.

The starting material for the solar cell is a Te-doped boat-grown n-type GaAs substrate. A p(GaAs) layer followed by a p( $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ) layer, both doped with Ge, were grown onto the substrate successively by using a horizontal LPE growth system. The grown samples were subsequently processed into cleaved or mesa cells. The p-n junction of the cell was identified from the peak of the beam-induced current trace, which was superimposed on the secondary emission image of the cleaved edge of the cell. The results show that the p-n junction is coincident with the substrate-grown layer interface, indicating that no apparent impurity cross diffusion had occurred during the growth period. With a slow cooling rate of  $0.2^\circ\text{C}/\text{min}$ , the thickness of the grown layers can be controlled within  $\pm 0.1 \mu\text{m}$  of the desired value. This technique provides good control of the position of the p-n junction which is a principal parameter for high efficiency p( $\text{Al}_x\text{Ga}_{1-x}\text{As}$ )-p(GaAs)- $\text{n}^+(\text{GaAs})$  solar cells. It also provides precise control of the carrier concentrations in the grown layers.

A series of LPE p(GaAs:Ge) layers with different doping levels was grown on  $\text{n}^+(\text{GaAs:Te})$  substrates and processed into cleaved diodes. SEM beam-induced current techniques were used for determining the minority-carrier diffusion lengths in the grown layers. Our results show that as the carrier concentration increases from  $10^{16}$  to  $10^{18} \text{ cm}^{-3}$ , the electron diffusion length slowly decreases from 8 to  $5 \mu\text{m}$ . In LPE p(GaAs:Ge) with a doping density of  $1.3 \times 10^{18} \text{ cm}^{-3}$ , an electron diffusion length of  $5.1 \mu\text{m}$  was obtained. In a boat-grown p(GaAs:Zn) substrate with a carrier concentration of  $2 \times 10^{18} \text{ cm}^{-3}$ , the electron diffusion length was found to be  $1.55 \mu\text{m}$ . These diffusion length results show that Ge is superior to Zn as a p-type dopant.

Several completed cells were tested under bright sunlight. The cell areas ranged from  $0.1$  to  $0.45 \text{ cm}^2$ . For a power input of about  $90 \text{ mW cm}^{-2}$ , which was measured by a calibrated Si solar cell, the typical open circuit voltage was  $0.87$  to  $0.90 \text{ V}$ , short circuit current was  $15$  to  $20 \text{ mA cm}^{-2}$  and the fill factor varied from  $0.70$  to  $0.75$ . Power conversion efficiencies ranging from  $10$  to  $15$  percent were obtained.

After further reduction in the series resistance and the reverse saturation current, together with optimization of the cell parameters, conversion efficiencies in the range of 15 to 20 percent can be expected. This study indicates that grown junction GaAs solar cells have several technical advantages and are practical to construct.

(3) Growth and Properties of Semi-Insulating Liquid Phase Epitaxial GaAs

Research Associate: B. L. Mattes

Graduate Student: Y. M. Houn

This research program is aimed at establishing parameters (temperature, dopants, distribution coefficients, etc.) necessary for the growth of thin GaAs layers of high sheet resistance on semi-insulating GaAs substrates by means of liquid phase epitaxial (LPE) techniques. Since the high resistivity epitaxial layers can only be obtained at a critical temperature in a particular growth system, different materials in the system are being investigated to broaden the transition temperature range. In addition, the electrical properties of these layers are being measured in order to determine the electron transport mechanisms and to provide information for device applications.

Buffer layers for use in field effect transistors have been grown having carrier concentrations of  $2.5 \times 10^{12} \text{ cm}^{-3}$  and sheet resistivities of  $1.5 \times 10^7$  ohms per square.

(4) Fundamental Studies of AlGaAs-GaAs Heterojunctions with Applications to Au-AlGaAs-GaAs Schottky Barrier Solar Cells

Graduate Student: Y. D. Shen

The purpose of this project is to study the band structure and the interface states of AlGaAs-GaAs n-n heterojunctions and to develop an Au-(n)AlGaAs-(n)GaAs Schottky barrier solar cell having a conversion efficiency around 15 to 20% and superior radiation resistance. Incorporation of a thin  $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$  layer ( $<0.5 \mu\text{m}$  in thickness) should increase the open circuit voltage of the cell without lowering its short circuit current.

(5) Lattice Defects in Annealed GaAs and  $\text{Al Ga}_x\text{As}_{1-x}$  Single Crystals

Graduate Student: K. I. Chang

The purpose of this project is to study the nature of defects which are introduced near the surface of AlGaAs single crystals during high temperature annealing. This is a continuation of the work on GaAs crystals as given in publications numbered (2) and (3) by S. Y. Chiang and G. L. Pearson. The results of this study should have practical applications to crystal growth, alloy metal contacts, impurity diffusion and LED fabrication.

(6) Fundamental Material Studies for Improving the Efficiencies of III-V Heterojunction Solar Cells

Graduate Student: J. S. Kim

The development of  $\text{Al Ga}_x\text{As}_{1-x}$ -GaAs solar cells has raised the photovoltaic solar energy conversion efficiency to 15-20% under AMO conditions. It appears that the efficiency can be further improved by increasing the energy bandgap of the AlGaAs window layer. However, in doing so, the resulting lattice mismatch at the heterojunction causes an increase in the interface recombination velocity. This study attempts to clarify the problem and develop techniques for constructing maximum efficiency cells.

(7) Electrical Transport Properties of  $\text{Al Ga}_x\text{As}_{1-x}$ ,  $\text{Al Ga}_x\text{Sb}_{1-x}$  and  $\text{In Ga}_x\text{As}_{1-x}$  Single Crystals

Graduate Student: K. Jew

The purpose of this project is to systematically study free carrier transport in AlGaAs, AlGaSb and InGaAs single crystal layers prepared by liquid phase epitaxial techniques. The electronic parameters of interest are free carrier mobility, resistivity, impurity activation energy, trap energy levels and minority carrier diffusion length. The results obtained in this study should prove useful for device applications.



# Publications:

1. "Diffusion in Semiconductors", H. C. Casey and G. L. Pearson in Point Defects in Solids, Vol. II, Ed. by J. H. Crawford and L. M. Slifkin (Plenum Press, New York, 1975) pp. 163-255.
2. "Properties of Vacancy Defects in GaAs", S. Y. Chiang and G. L. Pearson, J. Appl. Phys. 46, No. 7, 2986 (July 1975).
3. "Photoluminescence Studies of Vacancies and Vacancy-Impurity Complexes in Annealed GaAs", S. Y. Chiang and G. L. Pearson, Journal of Luminescence 10, 313 (1975).
4. "Applications of Ternary III-V Compounds to High Speed Microwave Modulation", A. A. Immoirica and G. L. Pearson, IEEE Trans. on Electron Devices, ED-22, 829 (1975).
5. "Phase Studies in III-V, II-VI and IV-VI Compound Semiconductor Alloy Systems", M. Ilegems and G. L. Pearson, in Annual Review of Materials Science, Volume V (1975) pp. 345-371.
6. "Growth and Properties of Semi-Insulating GaAs", B. L. Mattes, Y-M. Hounq and G. L. Pearson, J. Vac. Sci. and Technol. 12, 869 (1975).
7. "A Study of the Long Wavelength Optic Phonons in  $\text{Ga}_{1-x}\text{Al}_x\text{Sb}$ ", G. Lucovsky, K. Y. Cheng and G. L. Pearson, Phys. Rev. B 12, 4135 (1975).
8. "Effects of Zn Cross-Diffusion on the Properties of  $n(\text{Al}_x\text{Ga}_{1-x}\text{As})\text{-p}(\text{GaAs})$  Heterojunctions", D. T. Cheung, C. C. Shen, and G. L. Pearson, J. Appl. Phys. 46, 5226 (1975).
9. "Grown Junction GaAs Solar Cells", C. C. Shen and G. L. Pearson, Proc. IEEE 64, 384 (1976).
10. "Grown Junction GaAs Solar Cells", C. C. Shen and G. L. Pearson, Technical Digest, IEEE International Electron Devices Meeting, December 1-3, 1975, pp. 99-101.
11. "Double Band Crossing in  $\text{GaAlSb}$ ", K. Y. Cheng, G. L. Pearson, R. S. Bauer and D. J. Chadi, Bull. Am. Phys. Soc. 21, 365 (1976).

#### 54. STUDIES OF THE DYNAMICS OF MOLECULES AND MACROMOLECULES IN LIQUIDS

R. Pecora, Associate Professor, Chemistry

##### Professional Associates:

Q.-H. Lao

##### Graduate Students:

S. R. Aragon\*

D. R. Bauer\*

S. E. Bott

C. W. Cornelius

L. P. Miller\*\*

\*Received Ph.D. during report period.

\*\*Received M.S. during report period.

##### Agency Support:

NSF-GP-38228X

NIH-1R01-GM-2251701

##### Technical Objective:

To formulate theories of and to develop experimental techniques for studying the dynamics and motions of molecules in condensed systems.

##### Approach:

Theories of molecular motions and experimental techniques are formulated in terms of time-correlation functions. Experimental studies are carried out using dynamic light scattering, Raman scattering, infrared-band shapes, fluorescence correlations and nuclear magnetic relaxation.

##### Research Report:

###### (1) Resonance-Enhanced Depolarized Rayleigh Scattering

Graduate Student: D. R. Bauer

The linewidth of resonance enhanced depolarized Rayleigh scattering has been observed for a series of diphenylpolyenes in  $\text{CCl}_4$  solution. Rotational correlation times have been measured for these

compounds down to concentrations of  $10^{-4}$  Molar.<sup>(1)</sup>

Our results indicate that these and analogous compounds might be used as "light scattering labels" in complex media such as biological membranes. A Rayleigh scattering experiment could, for instance, be used to observe the rotational motion of the "label" molecule in a membrane. This method would not have the disadvantages with respect to time scale that limit the application of techniques such as electron spin relaxation or fluorescence depolarization.

(2) Studies of Morphology and Fusion of Phospholipid Vesicles

Graduate Student: S. R. Aragon

Phospholipid vesicles are one of the major model systems used for the study of membranes.

During the past year, we have developed theoretical and experimental techniques for characterizing polydisperse dispersions of vesicles and for studying vesicle fusion.<sup>(2)</sup> Experiments will continue with the new research period.

(3) Fluorescence Correlation Spectroscopy

Graduate Student: S. R. Aragon

A general theory of fluorescence correlation spectroscopy including the effects of translational and rotational motions and chemical reactions has been formulated.<sup>(3)</sup> In addition, an apparatus to perform these experiments is presently under construction.

It is hoped to use this technique (along with resonance-enhanced light scattering) to study rotational motion in biological membranes.

(4) Light Scattering from Macromolecules

Professional Associate: Q.-H. Lao

Graduate Students: D. R. Bauer

S. E. Bott

C. W. Cornelius

(A) Studies of rotational motion of biological macromolecules in

solution are being performed by depolarized Rayleigh scattering. In particular, conformations and dynamics of the antibiotic gramicidin A have been studied in various solvents. Studies are also in progress on the dynamics of synthetic polypeptides in solution.

(B) Studies of intramolecular motions of synthetic polymers in solution are in progress. A study of both "local" and "long-wavelength motions" in a series of narrow fraction polystyrenes has been completed.<sup>(4)</sup> Work is now in progress extending these studies to substituted polystyrenes and other polymers such as polymethacryl methacrylate.

(5) Electrophoretic Light Scattering

Professional Associate: Q.-H. Lao

Graduate Student: S. E. Bott

An apparatus for performing electrophoretic light scattering experiments is under construction. This apparatus should allow us to simultaneously measure electrophoretic mobilities and diffusion coefficients of macromolecules in solutions as well as to analyze complex mixtures of molecules of differing charge to friction ratios.

Reference Publications:

1. "Resonance Enhanced Depolarized Rayleigh Scattering from Diphenylpolyenes" by D. R. Bauer, B. Hudson, and R. Pecora, J. Chem. Phys. 63, 588 (1975).
2. "Theory of Dynamic Light Scattering from Polydisperse Systems" by S. R. Aragon and R. Pecora, J. Chem. Phys. 64, 2395 (1976).
3. "Fluorescence Correlation Spectroscopy as a Probe of Molecular Dynamics" by S. R. Aragon and R. Pecora, J. Chem. Phys. 64, 1791 (1976).
4. "Depolarized Rayleigh Spectroscopy Studies of Relaxation Processes of Polystyrenes in Solution" by D. R. Bauer, J. I. Brauman and R. Pecora, Macromolecules 8, 443 (1975).

55. PHASE TRANSITION KINETICS

G. M. Pound, Professor, Materials Science and Engineering

Graduate Students:

B. A. Chin	M. R. Mruzik*
G. M. Michal	M. E. Thomas
J. Miyazaki*	N. H. Tsai

\*Received PhD during report period.

Agency Support:

NSF DMR 74-00320 A01

NASA NSG 2071

NSF/MRL through CMR

NSF/MRL through CMR - Thrust Program on Synthesis, Characterization and Properties of Noncrystalline Metallic Alloys

Technical Objective:

To gain a better understanding of the physics of phase transformations and other thermally activated rate processes of interest in materials science, metallurgy, mechanical engineering and meteorology.

Approach:

Theoretical and experimental investigations of homogeneous nucleation in condensation from the vapor and freezing of liquids, of heterogeneous nucleation on substrates and of other thermally activated rate processes.

Research Report:

- (1) Statistical Mechanical Calculation of Surface Tension and Structure for Lennard-Jones Argon

(with Mr. Jun Miyazaki, graduate student, and Dr. John Barker)

The surface tension of liquid argon was determined near the triple point using a Monte Carlo technique. The L-J 12:6 pair potential function was employed in our study to simulate the argon system and a surface tension value of 18.3 dyne/cm was obtained at 83.86°K. The advantage of our method is that the statistical error for the

determination of surface tension in this region is greatly decreased; the statistical error of 0.3 dyne/cm in our calculation is smaller than that of the previous Monte Carlo study, which uses a mechanical definition, by one order of magnitude. Our surface tension value was compared with the experimental value for argon and we found that our value is 36% higher than the experimental value. We believe that this discrepancy comes from the fact that the L-J 12:6 potential is not a realistic potential function to represent the interactions between argon molecules and that the effect of the triplet interactions, which was not considered in this work, is relatively large. The application of first order perturbation theory to the final molecular configurations of our calculation suggests that the use of the Barker potential including the triplet interactions will lead to a lower surface tension value which is very close to the experimental value.

This method is, at the present time, applicable only near the triple point where the number of molecules in the bulk vapor phase is negligible. The extension and generalization of this method to higher temperature regions and also to a liquid-solid interface study should be fruitful.

The Monte Carlo method was also applied to the direct evaluation of the chemical potential of liquid argon in the bulk phase. The grand canonical method and the Bennett method were used in this calculation and we have calculated the chemical potential at several isotherms. These two methods gave almost identical results. We also have clarified, through our calculation, the discrepancies existing between the results of Hansen and Verlet and those of Rowley in their liquid-vapor transition studies of L-J fluids.

Surface tension and chemical potential results were applied to capillarity theory. The free energies of argon clusters predicted by the capillarity approximation at several temperatures below the triple point were compared with the exact Monte Carlo results obtained by Lee et al. using the same Lennard-Jones constants. This comparison indicates that the Lothe-Pound theory including only rotational and translational

contributions agrees very well with the exact results. In other words, the replacement free energy is almost negligible for this system, and the contribution to the bulk surface tension from release of rotational correlation is also negligible. This agreement does not necessarily mean that the real argon clusters have the same properties, but we expect similar results. In this case again, the use of a realistic argon potential containing many body interactions for the cluster calculation should give more physical insight into nucleation theory.

(2) Phase Transformation by Spinodal Decomposition: A Molecular Dynamics Simulation

(with Mr. M. R. Mruzik, graduate student, Professor F. F. Abraham and Dr. D. E. Schreiber)

We have carried out a numerical molecular dynamics simulation of phase separation by spinodal decomposition of a single-component Lennard-Jones fluid. The spatial density variations during the early stages of the phase separation in the unstable region conclusively corroborate the predictions of Cahn's linear spinodal decomposition theory. We believe that this computer "experiment" yields the first direct observation of the highly connected morphology evolving from spinodal decompositions (SD). Until now, spinodal decomposition has been experimentally studied in "real" physical systems, such as glasses and metallic alloys, and binary fluids near the critical point.

Our computer experiment on phase separation of a classical fluid consists in solving the equations of motion for a microcanonical system of 1372 Lennard-Jones (L-J) atoms by numerical integration using an IBM 360/195 digital computer. We adopted the numerical procedures first developed by Verlet for his molecular dynamics experiments on the equilibrium properties of classical L-J fluids. The thermodynamic quantities are measured in the usual "reduced" units. Our system of atoms is enclosed in a cube of length  $L = 15.8$  atom diameters and reduced density  $\rho^* = 0.35$ , with the standard periodic boundary conditions being imposed in order to simulate an infinite fluid system. We make special note of the fact that the periodic

boundary prevents the occurrence of inhomogeneities of a size larger than the side of the box,  $L$ .

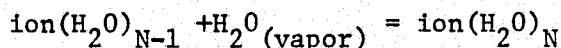
In large part, this experiment was made possible by recent advances in SD theory which elevated it from a phenomenological theory to a first-principles (microscopic) theory, and hence allowed us to determine the practicality and possible consequences of the experiment before attempting it. A generalized diffusion equation for SD has recently been derived using liquid-state perturbation theory for non-uniform fluids. Whereas Cahn predicts a linear dependence on  $R/\beta^2$  on  $\beta$ , where  $R$  is amplification factor and  $\beta$  is the wave number, Abraham predicts a significant nonlinearity. (A similar bending of the curve has been observed in x-ray studies of SD in glass systems and in a light scattering study of a binary fluid.)  $R(\beta_c) = 0$  gives the critical wavelength  $\lambda_c = 2\pi/\beta_c$  for the onset of exponential growth, and  $\lambda_c$  is  $4.8\sigma$ , well within the cutoff bound of  $L = 15.8\sigma$  imposed by the periodic boundary conditions in the molecular dynamics simulation.

We are presently extending the study to include the calculation of the far-field light scattering pattern, computationally a very time consuming calculation, and the simulation of SD in binary fluids.

### (3) Monte Carlo Study of Ion-Water Clusters

(with Mr. Mike Mruzik, graduate student, Dr. Donald E. Schreiber and Professor Farid F. Abraham).

The Procedures developed in this work have been employed to calculate theoretical free energies of formation of ion-water clusters for comparison with experiment. Gibbs free energies were calculated for the gas phase reaction:



for the  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ , and  $\text{F}^-$  ions and for  $N = 1$  to 6. The standard state for all calculations was taken as  $298^\circ\text{K}$  and 1 atmosphere. The Monte Carlo method was used to evaluate the appropriate classical expressions of statistical mechanics by employing the intermolecular potential functions recently developed from ab initio Hartree-Fock calculations. Enthalpies, entropies, and structural information were also



calculated. Agreement with experiment is sufficiently good to demonstrate the feasibility of this approach.

(4) Creep and Diffusion Coefficients in Solid Solution Alloys  
(with Mr. Bryan Chin, graduate student, and Professor W. D. Nix)

Existing theories have been used with success to predict the absolute creep rates in pure metals. Large amounts of experimental data are available to support these theories. However little success has been achieved by applying existing theories to predict creep rates in binary solid solution alloys. In reexamining the diffusional creep processes, some discoveries have arisen that offer the promise of exciting theoretical developments in the prediction of creep rates in solid solution alloys.

While measuring the creep rates of Al-Zn solid solution alloys, an unexpectedly large drop in the steady state creep rate was found upon addition of Zn at temperatures just above the miscibility gap. The measured stress exponent of the creep rate was found to decrease significantly while measured activation energy for the process increased by a factor of 2 upon increase of Zn composition. These observed changes cannot be accounted for by grain size, stacking fault, or modulus variations with composition.

It is proposed that this phenomenon is due to a change in the controlling creep mechanism from climb-controlled creep to glide-controlled creep. At the present time some controversy exists over the "appropriate" diffusion coefficient for climb and glide-controlled creep. In the course of the present work, a linked-flux analysis was applied to the problem of climb-controlled creep, and the appropriate theoretical diffusion coefficient was found to be precisely the Herring-Burton and Bastow Value

$$D_h = \frac{D_1^* D_2^*}{X_1 D_2^* + X_2 D_1^*}$$

where X is atom fraction and  $D^*$  is radioactive tracer diffusion coefficient.

A re-analysis of glide-controlled creep was also performed to determine the

appropriate theoretical diffusion coefficient, which was found to be the chemical diffusion coefficient

$$\tilde{D}_c = (X_1 D_2^* + X_2 D_1^*) \left[ 1 + \frac{d \ln \gamma}{d \ln X} \right]$$

where  $\gamma$  is the activity coefficient.

This diffusion coefficient shows a decrease upon addition of Zn which is of the magnitude needed to explain observed variations in the creep rate. Stress-exponent and activation-energy values are also consistent with the change from climb to glide-controlled creep. Thus for the solid solution Al-Zn, it is now possible to predict the absolute magnitude of the steady-state creep rate over the entire range of composition and temperature.

We believe that the present binary system, Al-Zn, is now the most completely understood in regard to its creep behavior. For example, it is much better understood than Au-Ni. Future work will be concerned with testing the applicability of the present theoretical approach to other solid solution alloys.

#### (5) Angstrom-Particle Catalysis

(with Mr. Mike Thomas, graduate student, and Professor Helmut Poppa)

Important examples of catalysis can be found in such areas as petroleum refining or automobile exhaust systems. Thus it is essential to evaluate and to predict a catalyst's performance, but at present there is no sound criterion for the design or evaluation of catalyst systems in terms of physical properties such as particle size and structure.

The catalyst being used in this experiment is Pd, which is vapor-deposited onto clean mica substrates in a vacuum on the order of  $10^{-10}$  torr. Substrate temperatures and vapor deposition rates are varied in order to generate thin films of catalyst crystallites having various sizes and crystallographic structures. Particle sizes, morphology and crystal structures are determined using a high resolution TEM, TED, and electronic image analysis. The size

distributions of the catalyst particles produced in various tests are evaluated from these data, using image computer techniques. The catalytic properties of the film will now be evaluated in-situ by localized reaction of a gaseous species, such as  $C_6H_6$ , on the catalyst surface in vacuum and analyzing the reaction products with a mass spectrometer. (The general type of chemical reactions studies will involve hydrogenolysis and a specific reaction will be selected which maximizes the influence of particle size (effects). In this way, the catalysts' performance will be evaluated by determining the rate and extent of reactions. Any changes in the catalysts' particle size over varying ranges of temperature and reaction time will also be studied, along with the possibility of selecting materials which will minimize "Ostwald Ripening" of the catalyst under high reaction temperatures. This ripening effect often reduces the catalytic activity severely.

(6) Computer Calculations and Simulations on Amorphous Metallic Alloys - A Part of the Glassy Metals Thrust Program

(with Mr. Nan-Hsiung Tsai, Mr. Gary Michal and Mr. Zimmer Jan, graduate students, and Dr. Troy Barbee and Professors F. F. Abraham, David Stevenson, and Arthur Bienenstock. Messrs. Tsai and Michal and Professors Abraham and Pound are directly involved in the computer part of this project.)

The purpose of this computer part of the Glassy Metals Thrust Program is to develop a predictive theory for the structure, structural anisotropy, void formation, crystallite formation, and formation of other defects in amorphous films by computer simulation methods. In the initial proposal, it had been planned to do this by molecular dynamic methods, ignoring the thermodynamic properties of the amorphous materials. However, within the past year, we have found that we can quench the alloys by Monte Carlo methods at any desired rate and determine the resultant structure and thermodynamic properties. This should prove to be a tremendous aid in reaching the goals of the entire Glassy Metals Program.

This Monte Carlo work has already begun, and we are in the process of trying to calculate the structure and thermodynamic

properties of amorphous niobium-nickel, copper-silver, and gadolinium-cobalt alloys as a function of quenching rate. In this work, the Lennard-Jones potential functions of Halicioglu and Pound are being used to approximate the properties of the actual metal atoms. This method has proven surprisingly successful in predicting the epitaxial relations and even the anisotropy of the epitaxy for deposition of gold, silver, copper and lead on tungsten, tantalum and molybdenum. The Monte Carlo system is comprised of five hundred to a thousand atoms, with periodic boundary conditions. We think it is important to emphasize that these very same amorphous alloys are being prepared by Dr. Barbee and his colleagues using sputtering techniques. Dr. Barbee's group will also undertake the electron microscopic characterization of the alloys. Professor Bienenstock and his group will use these specimens to determine the structure, including the radial distribution function, by X-ray diffraction techniques. His results will then be compared with the structures predicted by our theoretical computer calculations. Furthermore, using these same amorphous alloys, Professor Stevenson and his colleagues will measure the thermodynamic properties by E.M.F. Cell methods for comparison with our calculated thermodynamics results.

In the next phase of the work, we plan to undertake molecular dynamics simulations of the deposition of amorphous, multicomponent films, taking into consideration the mobility of the adatoms on the substrate surface and on the amorphous material itself, using the same systems named above, of course. At first, it is planned to use a hard-sphere model for the different-sized atoms. Then it is planned to use realistic values for both the binding potentials for the atoms and for the energies of activation for surface diffusion in the system. The variables will include composition of the thermal vapor beam, temperature of the thermal beam, orientation of the beam and temperature of the substrate. The resulting structures will be studied, and an attempt will be made to construct a predictive theory for the kinetic processes involved in deposition of amorphous films from the vapor.

An attractive possibility for the proposed computer work is the study of how "planned" irregularities in the substrate surface, such as micropits or crystallites of a third component, might be used to develop structural anisotropy in the direction normal to the film. This structural anisotropy is technologically very important, e.g., in the preparation of thin films for magnetic bubbles. At present, the origin of structural anisotropy in amorphous thin films is somewhat obscure. The present work offers the possibility of engineering structural anisotropy into amorphous thin films.

#### Reference Publications:

1. M. R. Mruzik, F. F. Abraham, D. E. Schreiber and G. M. Pound, "A Monte Carlo Study of Ion-Water Clusters", Journal of Chemical Physics **64**, 481 (1976).
2. F. F. Abraham, D. E. Schreiber, M. R. Mruzik and G. M. Pound, "Phase Separation in Fluid Systems by Spinodal Decomposition: A Molecular Dynamics Simulation", Physical Review Letters **36** 261 (1976).
3. T. Halicioglu and G. M. Pound, "Calculation of Potential Energy Parameters from Crystalline State Properties", Phys. Stat. Sol. a **30**, 619 (1975).
4. T. Surek, J. P. Hirth, and G. M. Pound, "The Screw Dislocation Spiral Mechanism of Crystal Growth and Evaporation", Proceedings of the Soviet Academy of Sciences (USSR) **11**, 203 (1975).
5. E. H. Lee, H. Poppa and G. M. Pound, "Quantitative Measurements of Nucleation and Growth Kinetics of Gold on Mica", Thin Solid Films **32**, 229 (1976).
6. F. F. Abraham, M. R. Mruzik and G. M. Pound, "The Thermodynamics and Structure of Hydrated Halide and Alkali-Ions", Discussions of the Faraday Society **61** (In Press).
7. W. D. Nix, D. M. Barnett, J. H. Holbrook, R. J. DiMelfi and G. M. Pound, "An Analysis of the Entropy of Thermally Activated Dislocation Motion Based on the Theory of Thermoelasticity", Phys. Stat. Sol. a (In Press).
8. K. Nishioaka and G. M. Pound, "Statistical Mechanics of Homogeneous Nucleation in Vapor", A chapter in "Nucleation", Volume II, edited by A. C. Zettlemoyer, Dekker, N. Y. (In Press).
9. J. Miyazaki, J. A. Barker and G. M. Pound, "Monte Carlo Calculation of the Surface Tension and Chemical Potential of Lennard-Jones Argon", J. Chem. Phys. **64**, 3334 (1976).

56. MICROWAVE ELECTRONICS

C. F. Quate, Professor, Applied Physics and Electrical Engineering

Graduate Students:

A. Albanese\*  
A. Atalar  
M. A. Hall  
V. B. Jipson\*\*

\*Received PhD during report period.

\*\*Received MS during report period.

Agency Support:

Navy N00014-75-C-0632  
Army DAHCO4-74-G-0093  
Hartford Foundation  
NSF ENG75-02028  
NSF APR75-07317  
NBS 5-35899

Technical Objective:

In this program we are concerned with the physical phenomena that underlies the propagation and radiation of acoustic waves over a spectrum of frequencies which extend to the microwave region. The devices and systems that evolve from our understanding of acoustic waves represent the goal of the complete program. We hope to devise systems which will exploit this form of radiation for the purpose of processing complex signals, of scanning optical images and direct viewing of microscopic images. The former two have been achieved and our current program is confined to the last item - the area of acoustic microscopy.

Research Report:

The Scanning Acoustic Microscope

Graduate Students: A. Atalar, M. Hall and V. Jipson

In the acoustic microscope we are using elastic waves to explore microscopic objects in a new way. The present instrument

exploits radiation with a wavelength of 1.5 microns to obtain a resolution that is less than one micron. It is, therefore, capable of viewing objects that are ordinarily seen with the optical instrument. However, most solids which are opaque to optical waves are transparent to acoustic waves. This new form of imaging should, therefore, permit us to view objects and structures which are not available in optical images.

With our present resolution ( $> 1$  micron) we are exploring the structural properties of integrated circuits and other devices which contain metallized layers. We want to determine if defects that are now hidden beneath the metallization can be examined with acoustic radiation. It is our present belief that with certain components and systems we will be able to quickly view features that now require elaborate and refined preparation techniques.

The instrument now operates with water at room temperature and it is the absorption in water that limits the resolving power. With a cooled instrument using simple monatomic liquids we should in principle be able to improve the resolving power by at least one order of magnitude. If this improvement is realized it will open up a realm in the solid state such as grain boundaries that have sub-micron dimensions.

#### Reference Publications:

1. R. A. Lemons and C. F. Quate, "Acoustic Microscopy - a Tool for Medical and Biological Research", Acoustical Holography, vol. 6, N. Booth, Ed., 305 (Plenum Press, New York, 1975).
2. W. L. Bond, C. C. Cutler, R. A. Lemons and C. F. Quate, "Dark Field and Stereo Viewing with the Acoustic Microscope", Appl. Phys. Lett., 27, 270 (1 September 1975).
3. J. Attal and C. F. Quate, "Investigation of Some Low Ultrasonic Absorption Liquids", J. Acoust. Soc. Am., 59, 69 (January 1976).

57. INVESTIGATION OF THE MICROMECHANICS OF EXPANSIVE REACTIONS IN CONCRETE

C. W. Richards, Professor, Civil Engineering

Graduate Students:

D. A. Burciaga

A. Kerdegari\*

\*Received Engineer Degree during  
report period.

Agency Support:

NSF ENG 74-23775

Technical Objectives:

To improve our understanding of expansive processes, particularly those associated with the calcium sulfoaluminate reaction in expansive cements, with the ultimate aim of making possible the wider use of these materials in the construction industry.

Research Report:

To aid in identifying the important variables in the expansive process a model has been developed for both free and restrained expansion. To investigate the effects of these variables we have experimented with blends of components of varying chemical compositions and varying particle size distributions. In the experiments we have monitored the depletion of sulfates in the cement-water mixture, the free expansion of thin paste slabs, and the restrained expansion of thin slabs and standard mortar bars. We have also studied the expansion of pastes during the first few hours after mixing, to correlate with the rapid depletion of sulfates that occurs at these early ages.

Current Research Program:

A computer program has been developed with which various particle size distributions can be simulated in the model. This will make it possible to scan the possible range of particle size distributions and select a distribution for optimum performance.



## 58. PROTEIN ADSORPTION TO POLYMER FILMS

C.R. Robertson, Associate Professor, Chemical Engineering

### Graduate Students:

M.P. Bohrer  
R.W. Bradshaw\*  
R.L.S. Chang\*  
G.L. Gussis

D.S. Inloes  
B.K. Lok  
V.M. Sanjana\*  
R.W. Watkins

\*Received Ph.D. during report period.

### Agency Support

ACS-PRF 7295-AC4, 7  
NIH 9 R01 AM 18910-04  
Engineering Foundation RC-A-73-5  
Veterans Administration

### Technical Objective:

To develop a new technique for the quantitative investigation of protein adsorption to polymer films.

### Research Report:

#### Protein Adsorption to Polymer Films

Graduate Student: R.W. Watkins

The initial event upon contact of blood with an artificial surface is the immediate deposition of a layer of plasma proteins. Often the compatibility of such a surface may be correlated to the type and amount of protein originally deposited. For this reason, protein adsorption to several important materials is being studied using a total internal reflection fluorescence technique. Based on the same physical principles as Multiple Attenuated Infrared Spectroscopy, the adsorption of a fluorescently labeled specie (in this case a protein--fluorescein isothiocyanate complex) may be followed continuously.

Initial experiments using this technique are devoted to developing adsorption isotherms for protein adsorption under both static and laminar flow conditions. Later studies will be expanded to cover a broader range of biomaterials and adsorption conditions.

59. SPECTROSCOPY AND QUANTUM ELECTRONICS

A. L. Schawlow, Professor of Physics

T. W. Hänsch, Professor of Physics

Professional Associates:

I. Knyazev (USSR), Visiting Scholar

G.H.C. New (England), Visiting Research Affiliate

R. Wallenstein (Germany), Visiting Scholar

W.M. Yen (University of Wisconsin), Visiting Research Affiliate

Graduate Students:

J. Eckstein

R. Feinberg

J. Goldsmith

R. T. Hawkins

M. E. Kaminsky\*

F. V. Kowalski

S. A. Lee\*

R. E. Teets

C. E. Wieman

\* Received Ph.D. during report period.

Agency Support:

NSF GP-14786

U.S. Navy ONR 71

USDC NBS4-9002-A1

Technical Objective:

To study the interaction between electromagnetic radiation and matter, to extend the range of coherent light techniques, to apply coherent and conventional light to elucidate problems in atomic, molecular and solid state physics.

Approach:

High resolution spectroscopy and fast-pulse electro-optical systems, using lasers where appropriate.

Research Report:

- (1) High Resolution Two-Photon Spectroscopy in the  $^1B_{2u}$  State of Benzene  
Visiting Scholar: R. Wallenstein

Highly resolved rotational spectra of two-photon excited vibrational levels in the  $^1B_{2u}$  state of  $C_6H_6$  and  $C_6D_6$  have been recorded

for linear and circular polarization of the exciting laser radiation, generated with a powerful narrowband dye laser system. The theoretical spectra fitted in collaboration with J. R. Lombardi (City College, City University of New York) are in excellent agreement with the experimental results and provide molecular parameters (rotational constants, Coriolis constants and structural parameters) of considerably improved accuracy.

(2) Identification of Absorption Lines by Modulated Lower-Level

Population: Spectrum of Na<sub>2</sub>

Graduate Students: M. E. Kaminsky

R. T. Hawkins

F. V. Kowalski

Molecular absorption lines from a common lower level are intensity modulated by chopped-laser saturation of another line from that level. Populations of some other levels are also modulated by subsequent fluorescence. Both types of modulated lines are free of Doppler broadening. Also, collisional depopulation modulates absorption from rotational levels near the laser-depleted level. In Na<sub>2</sub>, we have identified 113 lines. Analysis of the A state by Kusch and Hessel is confirmed and extended.

(3) Doppler-Free Laser Polarization Spectroscopy

Graduate Student: C. Wieman

We have demonstrated a sensitive new method of Doppler-free spectroscopy, monitoring the nonlinear interaction of two monochromatic laser beams in an absorbing gas via changes in light polarization. The signal-to-background ratio can greatly surpass that of saturated absorption. Polarization spectra of the hydrogen Balmer- $\beta$  line, recorded with a cw dye laser, reveal the Stark splitting of single fine structure components in a Wood discharge.

(4) Measurement of Relaxation Times and Cross Sections for Repopulation of Depleted Molecular Ground States

Graduate Students: R. Feinberg

R. Teets

Two tunable pulsed dye lasers are used to depopulate and probe a specific level in the ground state band of diatomic molecules immersed in a buffer gas. By delaying the probe pulse and monitoring its transmission for various delays, the repopulation lifetime and collision cross sections can be measured.

The first pulsed dye laser, of wavelength in the neighborhood of 4880Å, is directed through a heat pipe oven containing variable partial pressures of sodium and argon. This laser is used to strongly pump a chosen transition of the form  $X(v'', J'') \rightarrow B(v', J')$  thus heavily depleting the population of the  $(v'', J'')$  level of the ground state band of molecular sodium.

The radiative lifetime of the  $(v', J')$  levels of the B band is about 7 nanoseconds, rendering internal relaxation in this band negligible and making fluorescence down to many levels of the X band the only major pathway of decay. Therefore, after several radiative lifetimes, the B band is unpopulated, the  $(v'', J'')$  level of the X band is still depleted, and the population of many of the other X band levels are each very slightly increased.

After these conditions are established, a second, less intense pulsed dye laser tuned to the same transition (or any other transition having the same lower state as the pumping transition) is sent through the oven and allowed to weakly probe the volume of molecules which has previously been pumped. The time delay between the firing of the pump and probe pulses can be varied from zero to several hundred thousand nanoseconds using an electronic delay generator to control the triggering of the two lasers.

The transmission of the probe pulse will depend on the number of molecules in the  $(v'', J'')$  level which in turn depends on the repopulation rate and cross sections of sodium-sodium and sodium-argon collisions. By measuring the transmission for various probe delays, the lifetime for

repopulation can be determined. The argon pressure is then varied and a graph of repopulation rate vs. buffer pressure is drawn, allowing these cross sections to be found.

(5) Rapid, Precise, Digital Measurement of Laser Wavelength

Graduate Students: F. V. Kowalski

R. T. Hawkins

A method of measuring wavelength, accurate to one part in  $10^6$  and useful for cw lasers, is introduced. The instrument is a Michelson type interferometer. As one arm of the interferometer is moved, fringes from a known and unknown wavelength source are counted. The ratio of the counts is then the ratio of the wavelengths. Index of refraction corrections are of second order and can be neglected to this accuracy. Smooth mirror motion is obtained by mounting a corner reflector on an air track. In this method, the speed of motion, or even its constancy, is unimportant. The two beams traverse the same path through the interferometer in opposite directions, so that operation can be obtained even when the unknown wavelength is close to that of the standard. Iodine transitions near the Argon and Krypton laser lines are measured.

(6) Lower Level Labeling of Laser-Induced Polarization Effects

Graduate Students: R. E. Teets

R. Feinberg

Polarization spectroscopy<sup>1</sup> has been applied to the method of lower level labeling<sup>2</sup> to provide a useful technique for unraveling the complexities of molecular spectra. The resulting spectra resemble those from laser-excited fluorescence, but they provide direct information about the spectroscopic constants and quantum numbers of the upper state rather than the lower state.

Molecular sodium in an oven at 300°C was placed between crossed polarizers and illuminated with a broad band pulsed dye laser probe ( $\Delta\lambda \approx 300\text{\AA}$  centered at 4880Å). A pulsed circularly polarized saturating beam ( $\Delta\nu = 1\text{ GHz}$ ) tuned to a molecular transition ( $X \rightarrow B$ ) differentially depleted various angular momentum sublevels. Birefringence and dichroism

were thus induced in the molecular sample. This changed the probe polarization at those frequencies which interact with the lower level of the pumped transition. Light at these frequencies, corresponding to all transitions which have the same lower level as the pumped transition, was then able to pass through the crossed polarizers and be analyzed in a spectrograph.

The exact theory for saturation with intense pulses is somewhat complicated, but the following predictions can be made. The signal is proportional to the probe intensity and to the square of the pump intensity. However, for very high pump intensity, the various angular momentum sublevels tend to become equally depleted and the effect diminishes. For the large  $J$  values typical in molecular spectroscopy the  $\Delta J = \pm 1$  transitions should have equal intensities while the  $\Delta J = 0$  transition intensity should be reduced by a factor of  $1/J^2$ .

The observed spectra are consistent with these predictions. For  $\text{Na}_2$ , a typical spectrum has about ten evenly spaced doublets. The spacing between adjacent doublets gives the upper level vibrational spacings  $\omega$ , while the separation between components of a doublet is  $4BJ$  where  $B$  is the upper state rotational constant. The upper state vibrational quantum number can usually be inferred from the spectrum. Thus upper state constants and quantum numbers can be measured much more simply than by previous methods.

This method can simplify the analysis of an unknown atomic or molecular spectrum. It could also be helpful in studying transitions from specific ground-state levels to dissociation edges.

<sup>1</sup>C. Wieman and T. W. Hänsch, Phys. Rev. Letters 36, 1170 (1976)

<sup>2</sup>M. E. Kaminsky, R. T. Hawkins, F. V. Kowalski, and A. L. Schawlow, Phys. Rev. Letters 36, 671 (1976).

Reference Publications:

- (1) W. M. Yen, Tunable Gamma Ray Generation, Opt. Comm. 16, 5 (1976).
- (2) S. A. Lee, R. Wallenstein, and T. W. Hänsch, Hydrogen 1S-2S Isotope Shift and 1S Lamb Shift Measured by Laser Spectroscopy, Phys. Rev. Letters 35, 1262 (1975).
- (3) J. R. Lombardi and R. Wallenstein, High Resolution Two-Photon Spectroscopy in the  $1B_{2u}$  State of Benzene, J. Chem. Phys. (1976), submitted for publication.
- (4) M. E. Kaminsky, R. T. Hawkins, F. V. Kowalski, and A. L. Schawlow, Identification of Absorption Lines by Modulated Lower-Level Population: Spectrum of Na<sub>2</sub>, Phys. Rev. Letters 36, 671 (1976).
- (5) C. Wieman and T. W. Hänsch, Doppler-free Laser Polarization Spectroscopy, Phys. Rev. Letters 36, 1170 (1976).

## 60. INTERACTIONS OF ACOUSTIC RADIATION WITH SOLIDS

H. J. Shaw, Adjunct Professor and Associate Director,  
Edward L. Ginzton Laboratory

### Professional Associates:

W. L. Bond  
D. K. Winslow  
L. T. Zitelli

### Graduate Students:

H. Arditty	W. P. Leung
K. N. Bates	G. A. Pavlath
Le Nhon Bui	J. Souquet

### Agency Support:

AF	F30602-74-C-0038
AF	RI74-20773
Army	DAHCO4-74-G-0093
NSF	ENG72-04217A01
NSF	ENG74-00334
Navy	N00014-75-C-0632
Navy	N00123-74-C-1385

### Research Report:

Measurements have been made of the acoustic loss factor and piezoelectric coupling coefficient of poled  $\text{PVF}_2$  plastic polymer films which are of interest for high frequency ultrasonic applications. A theory for piezoelectric resonance in unsupported films was developed for interpretation of the measurements. Unloaded acoustic  $Q$  of approximately 14 has been observed at frequencies of 41 and 21.5 MHz for films of 25 and 50  $\mu$  thickness, respectively.

Broadband ultrasonic transducers using  $\text{PVF}_2$  piezoelectric plastic films, combining efficient transduction with extremely wide and uniform pass bands, have been fabricated using very simple procedures without any critical tolerances. Frequency spectra of impulsed transducers using films of 25  $\mu$  and 50  $\mu$  thickness, centered at 10 MHz and 5 MHz, respectively, are shown.



Work has continued on grating acoustic scanners, in which a chirped surface acoustic wave is converted into a focused, scanning bulk wave beam by coherent scattering from an array of parallel grooves. These devices can operate in both transmitting and receiving modes, to produce acoustic images of objects in real time. New models have been constructed, to evaluate their applicability to the study of defects in materials, with resolution of approximately 5 mm, and operating in the vicinity of 2 MHz.

Grating acoustic scanners have unique potential for producing electronically focused and scanned acoustic beams at very high frequencies, to obtain high resolution, as required, for example, in studying defects in ceramics. We have constructed a model using a grating consisting of ion etched grooves on a lithium niobate crystal. Operating at 140 MHz, it produces a line focus of 4 mil width over a 6 mm field of view in the focal plane. The theory for these devices shows that they are capable of both linear and section scanning.

Phase contrast imaging, which has been widely used in optical imaging for years, has recently been introduced into acoustic imaging, in systems using mechanical scanning. A phase contrast imaging system is being developed which employs electronic scanning and focusing. Differential phase contrast imaging is used, which compares the phases at adjacent points on the object which are separated by a constant distance along the scan line. The advantage of differential phase contrast imaging, as compared to fixed reference phase contrast imaging, is that the reference and signal beams travel almost identical paths, suppressing the effects of vibration, temperature, and other external influences. The present system consists of an acoustic receiver using a 100 element PZT array operating in the vicinity of 3 MHz, which has two identical main beams separated slightly in space, focused at the same distance and scanned simultaneously. The relative phases between the two beams can be varied, and for "dark field" imaging they are set  $180^\circ$  out of phase. The output of the receiver then reproduces either the phase distribution across the object, or its spacial derivative. Two dimensional differential phase contrast images are obtained by

adding a mechanical frame scan. The phase sensitivity is  $12^\circ$ , and the ultimate objective is a few degrees, for use in studying inhomogeneities in materials.

An acoustic linear Fresnel phase plate has been synthesized on an array of PZT acoustic transducers using binary digital electronics for signal processing. This approach allows the construction of a simple and flexible electronically scanned acoustic imaging device. Measurements have been made of the acoustic beam characteristics, and transmission images of a simple test pattern have been obtained with the system.

A new digital signal processing system has been designed which can be used to supply the signals required by acoustic imaging systems using PZT ceramic transducer arrays for non-destructive testing of materials. Independent, multilevel amplitude and phase requirements for all acoustic elements, for arbitrary electronic focusing and scanning of the acoustic radiation pattern of such arrays in real time, in either transmitting or receiving modes, are supplied. Prototype circuits are under construction. Final models will be tested as alternatives to analog tapped surface acoustic delay lines on BGO crystals which are presently used for supplying focusing and scanning signals for several types of PZT imaging devices.

Work was completed on a new type of surface acoustic waveguide to improve the transverse resolution in an acoustically scanned optical imaging system. The basic imaging device is the separated-medium, semiconductor convolver; optical patterns projected onto the semiconductor sensor are scanned by the acoustic surface wave. A waveguide formed by etching a narrow ridge on the surface of the Si wafer is employed to confine the surface wave beam and improve resolution transverse to the scanning direction. A significant improvement in resolution is demonstrated in a two-dimensional scan of an optical resolution test pattern. Cross-talk between adjacent parallel guides has been studied; reduction of cross-talk or resolution element size requires limiting the effects of carrier diffusion at the Si surface.

Work is continuing on a new type of analog-to-digital converter using surface acoustic waves on bismuth germanium oxide crystals, involving a basic property of surface acoustic wave transducers which has not heretofore been applied. It operates by comparing a reference signal, having a linearly varying amplitude versus time, with the analog input signal whose amplitude is to be digitized. The present device differs from standard integrating-type A/D converters in that the reference signal is produced by passing an rf tone pulse through an interdigital surface acoustic wave transducer which, because of its basic convolution property, can produce an accurate linearly varying ramp. This process offers a potential advantage in terms of temperature stability. An integrated circuit comparator is used to relate the amplitude of a sampled analog bit from the analog signal to the ramp amplitude, and an integrated circuit counter then outputs the corresponding digital count. The principle of the device was verified in an initial experiment with four-bit word capacity. We have since designed a two-channel model, with each channel having a conversion capacity of eight-bits in 2  $\mu$ sec, with parallel processing capability, to study the feasibility of using SAW A/D conversion with accuracy and throughput rates consistent with those other types of converters. Construction of this device is underway.

Work has continued on surface acoustic wave delay lines on piezoelectric crystals, having time delays up to 1 millisecond and bandwidths up to 60 MHz. The processing techniques for preparing the crystal plates is of utmost importance, and our work in this area has resulted in the development of successful techniques. We have found that interdigital surface acoustic wave transducers deposited on glass substrates and positioned very close to a piezoelectric crystal delay line surface ("spaced transducers") may be used to simulate identical transducers fabricated directly on the surface, for pretesting and prealignment of SAW devices. A novel spaced transducer mounting technique has been developed that utilizes a free floating gimbal, which permits positioning the spaced transducer substrate next to the delicately polished SAW substrate without damaging the surface polish. A treatment of the elec-

trical and acoustic coupling properties of the spaced transducers has been carried out. A phase bridge utilizing surface acoustic waves has been developed which measures small circumference variations of piezoelectric crystal cylinders of arbitrary cross-sectional shape, giving the actual "acoustic" circumference at any location. When used together with the spaced transducer, it is found that changes in the total acoustic circumference can be related to minute topographical variations of the surface such as regions of different crystalline composition, cracks, scratches, and geometrical misalignments. This technique is capable of very high precision, and the measurements using this technique could not be performed using standard optical and mechanical methods.

#### Reference Publications:

1. J. Fraser, J. Havlice, G. Kino, W. Leung, J. Shaw, K. Toda, T. Waugh, D. Winslow, and L. Zitelli, "An Electronically Focused Two-Dimensional Acoustic Imaging System," Microwave Laboratory Report No. 2445, Stanford University (May 1975); Acoustic Holography, Vol. 6, 275-304 (Plenum Press, New York, 1975).
2. C. M. Fortunko and H. J. Shaw, "One Millisecond Surface Acoustic Wave Delay Line," Ultrasonics Symposium Proceedings, p. 537, September 22-24, 1975.
3. A. Rønnekleiv, J. Souquet, and H. J. Shaw, "Grating Acoustic Scanners," Ultrasonics Symposium Proceedings, p. 91, September 22-24, 1975.
4. W. P. Leung, R. A. Mills, H. J. Shaw, D. K. Winslow, and L. T. Zitelli, "Non-Destructive Testing with an Electronically Focused Acoustic Imaging System," Ultrasonics Symposium Proceedings, p. 84, September 22-24, 1975.
5. P. L. Adams, H. J. Shaw, D. K. Winslow, and L. T. Zitelli, "Waveguides for Transverse Resolution in Surface Acoustic Wave Optical Sensors," Ultrasonics Symposium Proceedings, p. 153, September 22-24, 1975.
6. W. L. Bond, C. C. Cutler, R. A. Lemons, and C. F. Quate, "Dark-Field and Stereo Viewing with the Acoustic Microscope," Microwave Laboratory Report No. 2455, Stanford University; Appl. Phys. Letters 27, 5 (1 September 1975).

7. W. Bond, "Tuning Forks and Tuning Loops as Driving Elements," Microwave Laboratory Report No. 2461, Stanford University (July 1975).
8. K. N. Bates and H. J. Shaw, "An Acoustic Linear Phase Plate with Digital Electronic Scanning," Microwave Laboratory Report No. 2513, Stanford University (December 1975).
9. H. J. Shaw, "Degradation in Noise Figure along a Chain of Noisy Networks," Microwave Laboratory Report No. 2519, Stanford University (January 1976).
10. P. L. Adams and H. J. Shaw, "Low Loss  $\Delta v/v$  Waveguides," Edward L. Ginzton Laboratory Report No. 2535, Stanford University (February 1976).
11. W. L. Bond, C. M. Fortunko, S. L. Quilici, and H. J. Shaw, "Surface Acoustic Wave Probing with Spaced Transducers," Edward L. Ginzton Laboratory Report No. 2536, Stanford University (February 1976); accepted for publication in Rev. Scientific Instruments.
12. A. Rønnekleiv, H. J. Shaw, and J. Souquet, "A High Resolution Scanning Acoustic Beam at 140 MHz using a Surface Wave Grating," Edward L. Ginzton Laboratory Report No. 2537, Stanford University (February 1976).
13. A. Rønnekleiv, H. J. Shaw, and J. Souquet, "Theory of Sector Scanning with Grating Acoustic Scanners," Edward L. Ginzton Laboratory Report No. 2538, Stanford University (February 1976).
14. A. Rønnekleiv, H. J. Shaw, and J. Souquet, "Experimental Acoustic Surface-Wave to Bulk-Wave Scattering by Grooves," Edward L. Ginzton Laboratory Report No. 2539, Stanford University (February 1976); to be published in Electronics Letters.
15. A. Rønnekleiv, H. J. Shaw, and J. Souquet, "Grating Acoustic Scanners," Appl. Phys. Letters 28, 7, 361 (1 April 1976).
16. L. A. Coldren and H. J. Shaw, "Surface Wave Long Delay Lines," Proc. IEEE 64, 5, 598-609 (May 1976).
17. L. Bui, H. J. Shaw, and L. T. Zitelli, "Experimental Broad-band Ultrasonic Transducers using PVF<sub>2</sub> Piezoelectric Film," Edward L. Ginzton Laboratory Report No. 2573, Stanford University (May 1976); submitted to Electronics Letters.
18. L. Bui, H. J. Shaw, and L. T. Zitelli, "Study of Acoustic Wave Resonance," Edward L. Ginzton Laboratory Report No. 2570, Stanford University (May 1976); Submitted to IEEE, CU.

## 61. MECHANICAL BEHAVIOR OF SOLIDS

O. D. Sherby, Professor, Materials Science and Engineering

### Research Associates:

A. K. Miller  
H. Sunada  
J. Wadsworth  
R. Whalen

### Graduate Students:

R.D. Caligiuri	J. H. Lin
C. J. Shih	J. T. Lo
L. E. Eiselstein**	C. G. Schmidt
E. S. Kayali*	R. A. White
R. H. Klundt	

\*\* Received Master's degree during report period.

\* Received Ph.D. degree during report period.

### Agency Support:

ARPA N00014-75-C-1171 through CMR  
Navy N00014-75-C-0662  
N00014-75-C-0923  
NASA-NGR-05-020-671  
ERDA AT(04-3)-326 PA-38  
Electric Power Research Institute

### Research Report:

(1) Mechanical Behavior of Composite Materials  
(with John C. Shyne, Professor, Materials Science and Engineering)

### Graduate Students:

Che-Jen Shih  
L. Eiselstein  
R. Whalen (Research Associate)

### Technical Objective:

The program centers on the mechanical behavior of particulate composite materials, with special emphasis on the influence of hard particles on the strength and ductility of polycrystalline metals.

### Approach:

Techniques are being developed for the preparation of composite materials by powder metallurgy methods. Use is being made of a mechanical attritor for refining and mixing of powders prior to sintering and of a hydrostatic extrusion press for mechanical working difficult

to shape particulate composites. The mechanical behavior of solids are being assessed by means of constant strain rate and constant stress creep tests. The elastic behavior of the composite materials also will be studied.

#### Progress:

The high temperature strength of metallic alloys can be improved by the addition of fine particles of a second hard phase. Research is underway on the mechanism of strengthening of magnesium composite materials. Composites of Mg-Fe, Mg-B and Mg-Li-B (with up to thirty per cent of the second hard phase) have been prepared by a unique powder metallurgy-mechanical comminution processing treatment developed at Stanford University. In addition, we are investigating composites based on brass (70 Cu: 30 Zn) containing alumina particles.

Our research on large volume fraction composites has yielded new phenomena not previously reported. At low temperatures ( $<0.35T_m$ ) particles contribute to strengthening mostly through grain size refinement and partially through dispersion strengthening per se. At warm temperatures ( $0.35 - 0.6T_m$ ) particles can contribute to dispersion ductilizing when particles become active sources of dislocations and vacancies; this situation leads to high strain rate sensitivity, a factor that enhances tensile ductility. At high temperature ( $>0.6T_m$ ) the large volume fraction composites exhibit strain aging and yield point effects. In addition, a "threshold stress" appears to exist below which plastic flow apparently does not occur. Physical models to explain these effects are currently being developed.

Elastic property characteristics of composite materials are being assessed. Exceptionally high elastic stiffness materials have been prepared by the addition of boron particles to magnesium. A magnesium -25 v/o boron alloy has been developed with a modulus of  $11.4 \times 10^6$  psi. This value is about double that for most commercial magnesium alloys although the ductility is low (5% compression deformation is only possible before cracking occurs). Research is now being extended to Mg-Li solid solution alloys containing boron particles. Current results on a Mg-Li (15 at % Li) solid solution alloy containing 25 v/o boron have revealed

Promising mechanical characteristics: the elastic stiffness is over  $12 \times 10^6$  psi. The ductility of these composites in compression tests is high (no fracturing after 50% deformation) although the tensile ductility is low. The type of materials we have developed would suggest a new class of technologically useful materials, namely, particulate composites containing large volume fractions of hard second phase.

We have initiated research on a new class of particulate composite materials. This work introduces a new concept. Two constituents, in the form of powders, are mixed and pressed at a temperature where bonding occurs but no changes in structure of the two dissimilar powders occur. Such a composite is then heated to a temperature where selective heat treatment can occur, i.e. one of the constituents changes in structure and properties but the other does not. Preliminary tests on mixtures of powders consisting of pure iron and ultrahigh carbon steel suggests that such an approach permits the attainment of a wide range of unusual microstructures and properties.

## (2) Hydrostatic Extrusion

(with John C. Shyne, Professor of Materials Science and Engineering and Erastus H. Lee, Professor of Applied Mechanics)

### Graduate Students:

R. Caligiuri  
L. Eiselstein  
R. Mallett (Research Associate)  
R. Whalen (Research Associate)

### Technical Objective:

To determine the advantages and disadvantages of hydrostatic extrusion as a means of improving the properties of extruded materials. The frontier of hydrostatic extrusion in forming materials not extrudable by normal extrusion processes will be investigated. Comparison of hydrostatic extrusion with other large strain forming operations, such as wire drawing and rolling, will be made.

### Approach:

This research has as its aim the study, both analytical and experimental, of the mechanics of the hydrostatic extrusion process, and the application of hydrostatic extrusion to the preparation of wrought materials of superior properties.



## Progress:

We will be investigating the response of a variety of materials to hydrostatic extrusion. The microstructure and mechanical properties of extruded materials will be related to the important processing variables, extrusion ratio, extrusion pressure, temperature, and extrusion rate. The experiments fall into two categories: 1. A detailed, systematic investigation of the influence of the processing variables on the properties of several fairly simple materials (pure Fe, Ni, Mg, and Ti; and Cu-30Zn or Cu-10Sn) 2. The utilization of hydrostatic extrusion to optimize the properties of more complex materials chosen for their technological utility (Mg-Li-B for high specific stiffness; Fe-C for high strength, ductility; T-D Nichrome for high temperature strength; Al-Fe alloy for high strength, high conductivity material; NbTi a super conducting alloy).

The hydrostatic extrusion press is capable of extruding at pressures up to 500,000 psi. Extruded samples can be water quenched instantaneously upon exiting the die; this permits capturing the worked structure developed in the adiabatically heated samples. Preliminary studies on aluminum, containing dilute amounts of iron, have revealed development of ultrafine subgrain structures in samples extruded at a ratio of eighty one to one. The resulting products exhibit yield strengths in the order of 30,000 psi, a high value for such high conductivity aluminum alloys.

The theoretical portion of the program is devoted to an understanding of the mechanics of extrusion. Elastic-plastic finite-element programs are being considered as a means of analyzing the extrusion process. Such studies are directed towards a complete stress analysis of extrusion and should lead to a better elucidation of the factors influencing the onset of undesirable defects during extrusion.

### (3) Deformation of Materials at High Strain Rate at Warm and High Temperatures

#### Graduate Students:

R. Caligiuri  
S. Kayali  
R. Klundt  
C. Schmidt  
R. White

#### Technical Objective:

To study the mechanism of deformation at high strain rate at warm and high temperature. Study of the mechanical behavior of unusual structures developed by thermal-mechanical processing operations with special emphasis in the warm working range of temperatures where subgrains and/or fine grains are developed.

#### Approach:

Constant strain rate tests and special thermal-mechanical processing treatments are used with the objective of developing ultra fine structures. A rapid quenching technique during high strain rate torsional deformation has been devised to assess the deformation mechanisms of warm and hot working. Superplastic characteristics of fine grained materials are being studied by means of tension and compression testing.

- a. Development of controlled fine structures by thermal-mechanical processing. (warm working and superplasticity)

We have been attempting to develop particulate composites in ultra-high carbon steels by special thermal-mechanical treatment (TMT) processing. Our research has centered on plain carbon steels containing 1.0 to 2.3% carbon (twenty to thirty-five volume percent cementite respectively). Much of our basic studies in the past years related to strain-enhanced spheroidization, warm working, strain created vacancies and superplasticity proved indispensable in our attempt to obtain fine grained structures in ultrahigh carbon steels. Various TMT processing procedures have been developed which have resulted in particulate composites of cementite in iron containing ferrite grains finer than one micron in size. Such high carbon steels are superplastic at warm temperatures (over 750% elongation has been achieved). Furthermore, they can be made strong and ductile at room temperature. This is the first time plain carbon steels have been made superplastic and our results suggest exciting possibilities in the application of inexpensive steels for many new structural applications. In addition to exhibiting superplastic characteristics, the ultrahigh carbon steels can be heat treated to possess exceptionally high hardnesses. Thus the fine martensite needles that form from the prior fine austenite grains lead to steels with compression fracture strengths exceeding 600,000 psi.

We are investigating the influence of background impurity content (principally Mn and Si) on the superplastic characteristics of the ultrahigh carbon steels. Current results indicate that it is not possible to make such Fe-C alloys superplastic when they are pure; this unexpected result is attributed to the ease of grain growth in such materials. Dilute alloying with nickel, chromium and vanadium are being considered as a means of enhancing the superplastic properties of the ultrahigh carbon steels. Furthermore, such low alloyed ultrahigh carbon steels may exhibit exceptional properties after suitable heat treatment, and this aspect of our work will be emphasized.

The ease of deformation of superplastic materials would suggest that such materials, when in powder form, can be sintered readily under low pressures. We are investigating the sintering characteristics of such materials. Results on powders of a 2.6%C cast iron suggest that "superplastic warm pressing" is indeed a feasible method of enhancing the sintering process; present studies will include ultrahigh carbon steels which we have already shown to be superplastic.

b. Mechanism of warm and hot working in crystalline solids.

The factors influencing ductility and ductile fracture of materials at elevated temperature have not been studied extensively. Such studies are of paramount importance in assessing the formability of materials. A torsion apparatus has been developed at Stanford capable of deforming materials up to strain rates of 10,000 per cent per second and temperatures of up to 2200°F. One of the unique features of our apparatus is that samples can be quenched instantaneously after deformation. In this manner the exact mechanism of plastic flow during high strain rate deformation can be evaluated. We are also capable of simulating complex thermal-mechanical processing operations with small scale samples.

Our work has revealed that structural change during warm working of polycrystalline solids is characterized by the formation of well defined subgrains. The subgrain size developed depends primarily on the modulus compensated stress,  $\frac{\sigma}{E}$ , and is insensitive to solid solution alloying, crystal structure and stacking fault energy. The nature of the subgrain boundary, however, appears to be a function of the temperature at which it is formed. For a given subgrain size, the higher the

temperature of working the more effective is the subgrain boundary as a barrier to low temperature plastic flow. We have shown that subgrains can be a more potent method of hardening than grains in the fine size range (ten microns and less). Studies include austenitic and ferritic stainless steels as well as several iron base binary solid solution alloys. We are studying the influence of large plastic strain ( $\epsilon = 15$  to 20) at warm temperature on the development, and nature of subgrain boundaries. Preliminary results on a ferritic stainless steel suggest that creep properties, as well as room temperature properties are influenced by the amount of warm working strain. This processing variable (of large strain deformation) at warm and hot temperatures has generally not been considered in technological applications and has not been studied academically.

#### (4) Mechanical behavior of polycrystalline solids at elevated temperatures.

##### Graduate Students:

R. Klundt  
J. Lin  
A. K. Miller (Research Associate)  
C. Schmidt

##### Technical Objective:

To understand the mechanical behavior of polycrystalline solids at elevated temperature ( $0.4$  to  $0.9T_m$ ) under conditions of low stress (creep).

##### Approach:

Constant stress creep tests and constant strain rate tests are used to assess properties of both metallic and non-metallic polycrystalline solids.

##### Progress:

The importance of subgrains on the creep resistance of materials is not well understood. Our studies are directed at determining the contribution of subgrains to the creep process. Using stress-drop tests and change-in-strain-rate tests, it has been possible to determine the influence of strain rate on the flow stress at constant structure. Such tests also permit determination of the possible influence of subgrain size on the creep rate. Studies on pure aluminum, coupled with other

data, reveal that the creep rate can be given by  $\dot{\epsilon} = 10^{11} \frac{D_{\text{eff}}}{b^2} \left(\frac{\lambda}{b}\right)^3 \left(\frac{\sigma}{E}\right)^8$ .

Here  $D_{\text{eff}}$  is the effective diffusion coefficient,  $\lambda$  is the subgrain size,  $\sigma$  is the creep stress,  $E$  is the dynamic unrelaxed elastic modulus and  $b$  is burgers vector. There are no contemporary creep theories that can explain these results. The practical implications of our work is clear; if one can decrease the subgrain size by a factor of a hundred, the creep rate will decrease by a factor of a million. To retain fine subgrains for high creep resistance at a given stress it will be necessary to pin such boundaries. It is intended to investigate the influence of subgrains on the creep resistance of austenitic and ferritic steels.

We are attempting to determine the mechanism of creep flow in T-D Nichrome and other dispersion hardened materials. In this study, we are attempting to establish if a threshold stress for creep exists in T-D Nichrome since there is evidence for such behavior in high volume fraction dispersion hardened systems. Novel methods such as stress relaxation are being used to determine the stress exponent for creep as well as to determine the creep behavior at very low strain rates. Special emphasis will be placed on the possible importance of subgrain size and interparticle spacing on the creep resistance of T-D Nichrome; transmission electron microscopy will be used as a means of detecting the microstructure.

A phenomenological model to simulate the transient and steady-state deformation behavior of metals under complex load and temperature histories has been developed. Designated as MATMOD (for MATerials MODel), its major characteristics are (1) a unification of short-time plasticity, long-time creep, and cyclic deformation into a single set of constitutive equations, and (2) the use of metallurgical structure as a primary variable. The model has been tested on aluminum, stainless steels, and a nickel-base superalloy and is being developed further for use with Zircaloy and eventual implementation into nuclear reactor performance and safety analysis codes.

#### Publications and Presentations since June 1975

1. "Yield Points and Strain Aging in Hexagonal-Based Particulate Composites", I. C. Huseby, S. E. Hsu, T. R. McNelley, G. R. Edwards,

- D. Francois, J.C. Shyne and O.D. Sherby, Metallurgical Transactions, 6A, 2005 (1975).
2. "On The Influence of the Mode of Deformation on the Hardening of Iron at Low Temperature and Large Strains", C.M. Young, L.J. Anderson and O.D. Sherby, Metallurgical Transactions, 6A, 2164 (1975).
  3. "Diffusion Controlled Deformation of Particulate Composites", G. R. Edwards, T.R. McNelley and O. D. Sherby, Philosophical Magazine, 32, 1245 (1975).
  4. "Superplastic Hot Pressing of White Cast Iron", R.D. Caligiuri, R.T. Whalen and O. D. Sherby, The International Journal of Powder Metallurgy and Powder Technology, 12, 9 (1976).
  5. "On Subgrain Strengthening at High and Low Temperatures", Alan K. Miller and Oleg D. Sherby, Scripta Metallurgica, 10, 311 (1976).
  6. "Mechanical Behavior of Cadmium-Boron and Cadmium-Tungsten Particulate Composites", S.E. Hsu, G.R. Edwards, J.C. Shyne and O.D. Sherby, Journal of Materials Science, in press.
  7. "Superplastic Ultra High Carbon Steel", Oleg D. Sherby, Conrad M. Young, Bruno Walser and Eldon M. Cady, U.S. Patent 3,951,697, April 20, 1976.
  8. Invited presentations were given by Oleg D. Sherby on "Superplastic Ultrahigh Carbon Steels" to Lockheed Research Laboratory, Palo Alto (July 1975), Wesdex Annual Meeting, Los Angeles (Dec. 1975), Lawrence Livermore Laboratory (Jan. 1976), North American Rockwell Science Center, Thousand Oaks (Jan. 1976), Cleveland Chapter of AIME (April 1976).
  9. Invited lecture to ARPA Workshop on Sintering, on "Superplastic Warm Pressing", San Diego, July 1975. Similar lecture given by Robert Caligiuri to Western Metals Congress, Los Angeles (March 1976).
  10. Invited paper on "Flow Stress, Subgrain Structure and Subgrain Stability", O. D. Sherby, R. H. Klundt and A. Miller, 105th Annual Meeting, Las Vegas, Nevada, February 23, 1976.
  11. "An Inelastic Constitutive Model for Monotonic, Cyclic, and Creep Deformation: Part I - Equations Development and Analytical Procedures", A. Miller, Journal of Engineering Materials and Technology, 98, 97 (1976).
  12. "An Inelastic Constitutive Model for Monotonic, Cyclic, and Creep Deformation: Part II - Application to Type 304 Stainless Steel", A. Miller, Journal of Engineering Materials and Technology, 98, 106 (1976).

## 62. ULTRA-SHORT OPTICAL PULSE GENERATION AND APPLICATIONS

A. E. Siegman, Professor of Electrical

### Graduate Students:

J. R. Salcedo  
P. Zorabedian\*  
G. A. Hayward

H. C. Brayman  
A. J. Duerinckx

\*Received MS during report period.

### Agency Support:

AF F 44(620-71-C)0053  
NASA NGL-05-020-103  
NSF GK32371X

### Technical Objectives:

To generate the shortest possible picosecond light pulses on a continuous wave and tunable basis; and to use these pulses in making significant physical measurements on materials, particularly materials of biochemical and biophysical interest.

### Approach:

The development and use of a transient-grating picosecond light scattering technique, together with a repetitively Q-switched mode-locked laser, is being applied to the measurement of ultrafast physical and photochemical processes.

### Research Report:

Our group has made significant contributions over the past several years to the development of the laser mode locking techniques that make possible the generation of continuous trains of extremely short optical pulses (pulsewidths less than 30 psec). By using these extremely short optical pulses, both to excite atomic and molecular systems, and then to probe the changes in the optical properties (e.g., change in the complex susceptibility tensor) of the excited systems, one can potentially make

time resolved measurements of atomic and molecular properties (such as relaxation times and reorientation times) with picosecond time resolution. This degree of time resolution is inaccessible using conventional optical detectors and optical pulse measurement methods.

Picosecond pulses with high peak powers, have been achieved in the visible (5320 Å) and the UV (3547 Å, 2660 Å), as well as in the IR (1.064 μ). From this work, a theoretical understanding of the transient buildup of mode-locked pulses has been attained.<sup>1</sup> A LiNbO<sub>3</sub> electro-optic switch has been constructed to gate out a single pulse in each train of mode-locked pulses comprising each Q-switched pulse.

Two pulses from the same laser arriving at an experimental sample coincident in time but from slightly different directions can produce excited states or other photo-excited effects in the form of an induced grating or a transient hologram pattern in the sample. A variable-delay laser probe pulse can then be diffracted by the photo-induced grating.<sup>2,3,4</sup> By using a repetitive train of short pulses and measuring the diffracted probe beam intensity averaged over many pulses, while slowly varying the time delay between excitation and probe pulses, one can measure the decay of the photo-excited phenomenon in stroboscopic fashion, with a time resolution approximating the laser pulsewidth. We have now carried out preliminary measurements of molecular relaxation times using repetitive mode-locked laser pulses<sup>5</sup> plus such a transient-grating apparatus designed to measure a wide variety of subnanosecond to picosecond phenomena.<sup>6</sup>

Our apparatus uses a continuously pumped, repetitively Q-switched, actively mode-locked Nd:YAG laser<sup>5,6</sup> which produces bursts of 20 to 30 mode-locked pulses with several hundred kilowatts peak power and durations of ~ 60 psec at repetition rates up to 500 Hz. The pulses from this laser enter an optical system which produces two excitation beams and a variable-delay probe beam intersecting at a common point. Our transient-grating measurements to date



were made with two excitation beams separated by 53 mrad, together with a central probe beam, all focused to a  $\sim 70 \mu\text{m}$  gaussian spot size in a 125  $\mu\text{m}$  thick dye cell containing a  $10^{-4}$  M solution of Rhodamine 6G in methanol, ethanol or 1-propanol. The dye cell was rotated slowly to avoid photodecomposition of the dye. A transient grating with a 10  $\mu\text{m}$  spatial periodicity was produced in the dye cell by excitation by 532 nm from the ground singlet  $S_0$  to the first excited singlet state  $S_1$ . This grating could be photographed through a microscope by its own fluorescent emission.

Diffraction of the probe beam from this grating resulted from the difference in absorption cross-section of the  $S_0$  and  $S_1$  states for the 532 nm probe wavelength.<sup>7</sup> In fact, the two excitation beams by themselves first produced two strong self-diffracted beams located an additional 53 mrad outside each of the two incident beams. For any delay greater than zero the probe beam then produced two readily visible diffracted beams corresponding to the +1 and -1 orders of the induced grating produced by the excitation beams, as well as self-diffracted cross-product beams between the probe and each excitation beam.

The normalized intensity of one of the diffracted probe beams versus the probe pulse delay, time-averaged over many pulses, is proportional to the amplitude of the decaying transient grating squared times the incident pulse intensity  $P_0$ . For the dye solution studied in these experiments the grating amplitude depends on the decay of the population difference (and on the absorption cross-section difference) between  $S_0$  and  $S_1$  singlet levels, suitably averaged over the orientational distribution of the molecules.<sup>4,8,9,10</sup> The decaying portion of the scattered signal contains two times constants  $\tau_s$  and  $\tau_{\text{rot}}$ , where  $\tau_s$  is the upper singlet fluorescence lifetime and  $\tau_{\text{rot}} \equiv (6D_{\text{rot}})^{-1}$  is the orientational relaxation time.

Table I summarizes our results for Rhodamine 6G in three different solvents. Within experimental accuracy the rotational relaxation times agree with those measured by Chuang and Eisenthal.<sup>9</sup>

TABLE I

Experimental Results for the Singlet State Lifetime  $\tau_s$  and Rotational Relaxation Time  $\tau_{rot}$  for Rhodamine 6G in Several Alcohols

Solvent	R6G Concentration	$\tau_{rot}$	$\tau_s$
Methanol	$2.0 \cdot 10^{-4}$ M	$140 \pm 30$ psec	$1.7 - 2.0$ nsec
Ethanol	$1.0 \cdot 10^{-4}$ M	$300 \pm 50$ psec	$3.7 \pm 0.5$ nsec
1-Propanol	$1.0 \cdot 10^{-4}$ M	$500 \pm 100$ psec	$3.8 \pm 0.5$ nsec

Also, other experiments are being prepared, namely measurements of Kerr coefficients. A process of further shortening the 30-50 psec pulses is being also planned, by using a Gires-Tournois interferometer inside the laser cavity for pulse narrowing.

We believe the transient grating technique used here can be useful as a method of excited-state spectroscopy for a wide variety of similar experiments involving molecular states, excited states in semiconductors, excitons in molecular crystals, nonradiative relaxation rates, and energy transfer studies. Because one detects a small scattered probe signal against a dark background, rather than looking for a small change in a large (and possibly noisy) probe beam, the transient-grating method can offer improved sensitivity and background rejection. Because a phase grating will diffract the probe beam as well as an amplitude grating, one can probe excited-state dispersion as well as absorption effects. By varying the beam angles and thus the grating spacing, one can separate spatial diffusion from lifetime effects in the grating relaxation; and by rotating the fringe direction relative to the sample, one can study anisotropic diffusion effects.

At this stage of the research, we are preparing the experimental setup for exciton migration studies in molecular crystal at low temperatures, as well as several other excited state spectroscopy measurements in the picosecond range of these experiments, our most important research effort is the direct study of anisotropic diffusion of excitons in crystals, for which our technique appears to be especially suitable.

#### Reference Publications:

1. D. J. Kuizenga, D. W. Phillion, T. Lund, and A. E. Siegman, "Simultaneous Q-Switching and Mode-Locking in the CW Nd:YAG Laser," *Optics Comm.* 2, 22 (November 1973).
2. R. L. Carman, R. Y. Chiao, and P. L. Kelley, *Phys. Rev. Letter* 17, 1281 (1966); J. R. Woerdman and B. Bolger, *Phys. Letters* 30A, 164 (1969); P. Y. Key, R. G. Harrison, V. I. Little, and K. Katzenstein, *IEEE J. Quant. Electr.* QE-6, 641 (1970); H. Eichler, G. Salje, and J. Stahl, *J. Appl. Phys.* 44, 5383 (1973); D. R. Dean and R. J. Collins, *J. Appl. Phys.* 44, 5455 (1973); A. A. Borshch, et al., *JETP Letters* 18, 397 (1973); T. A. Wiggins and A. Salik, *Appl. Phys. Letters* 25, 438 (1974); T. Sawatari and D. M. Shupe, *Appl. Phys. Letters* 24, 95 (1974); J. Vaitkus, et al., *IEEE J. Quant. Electr.* QE-10, 699 (1974).

Contd. Reference Publications:

3. M. E. Mach, Phys. Rev. Letters 22, 13 (1960); W. Rother, H. Meyer, and W. Kaiser, Z. Naturforschung 25a, 1136 (1970); R. I. Scarlet, Phys. Rev. A 6, 2281 (1972); D. W. Polh, S. E. Schwarz, and V. Irniger, Phys. Rev. Letters 31, 32 (1973); C. V. Shank and D. H. Auston, private communication.
4. C. V. Shank and E. P. Ippen, Appl. Phys. Letters 26, 62 (1975).
5. D. J. Kuizenga, D. W. Phillion, T. Lund, and A. E. Siegman, Optic Comm. 2, 221 (1973).
6. D. W. Phillion, "Evolution of Mode-Locked Pulses and Their Application to Time Resolved Spectroscopy," Ph.D. Dissertation, Department of Electrical Engineering, Stanford University, Stanford, California 94305, November 1974.
7. O. Teschke and A. Dienes, Appl. Phys. Letters 26, 13 (1975).
8. K. B. Eisenthal and K. H. Drexhage, J. Chem. Phys. 51, 5720 (1969).
9. T. J. Chuang and K. B. Eisenthal, Chem. Phys. Letters 11, 368 (1971).
10. D. W. Phillion, D. J. Kuizenga, and A. E. Siegman, J. Chem. Phys. 61, 3828 (1974).

### 63. ELECTRON SPECTROSCOPY, SURFACES, AND INTERFACES

W. E. Spicer, Professor of Electrical Engineering and Materials Science  
and Engineering

#### Professional Associates:

J. S. Johannessen  
E. Fortin  
P. E. Gregory\*

I. Lindau  
R. A. Powell  
\*Received PhD during report period

#### Graduate Students:

P. W. Chye  
D. M. Collins  
C. M. Garner  
M. R. Kump  
D. T. Ling

J. N. Miller\*\*  
P. A. Pianetta  
P. M. Stefan\*\*  
K. Y. Yu\*

\*\*Received MS during report period

#### Agency Support

ARPA DAAK02-74-C-0069	NAVY N00014-75-C-0289
ARMY DAAG29-74-C-0022	ARPA THRU NBS 5-35944
ARMY DAHC04-74-G-0215	JSEP N00014-75-C-0601
NSF DMR74-22230 A1	EPRI RP 631
NSF/MRL through CMR- Thrust Program on Alloy Catalytic Materials	

#### Technical Objective and Approach:

To apply the newly developed tools of electron spectroscopy (Photoemission, Auger, etc.) together with other techniques such as temperature programmed desorption to the study of surfaces and interfaces. Particular attention is given to fundamental problems which can have strong practical impact, e.g., in catalysis and semiconductor devices.

#### Research Report:

##### (1) Studies of Cu/Ni Alloys Related to Catalysis

D. T. Ling and K. Y. Yu

As part of a larger program to study materials of catalytic interest, we have made extensive studies of the Cu/Ni alloy system using ultraviolet photoemission spectroscopy (UPS), Auger electron spectroscopy (AES), and thermal desorption spectroscopy (TDS). Recently

it has been noted that transition metal alloys will exhibit greater catalytic activity and superior selectivity in promoting certain desired chemical reactions as compared to the pure metals. A remarkably successful multimetallic catalyst is the "KX 130" reforming catalyst developed at Exxon. In our laboratory we have been particularly interested in investigating the fundamental physical processes involved in a catalyzed reaction and in distinguishing those characteristics which make a material a good catalyst. To that end we have combined a number of techniques of surface physics and studied the Cu/Ni alloy system. These techniques have allowed us to determine the surface composition and relate it to chemisorption phenomena.

Most recently we have complemented earlier UPS studies by examining the chemisorption of CO and H<sub>2</sub> on Cu/Ni alloys by TDS. The sample used was a (110) oriented single crystal having 10% Cu-90% Ni bulk atomic composition. However, by Ar<sup>+</sup>-ion sputtering the sample and then annealing for varying temperatures and times, the surface composition, as determined by AES, could be changed from 82% Ni-18% Cu to 35% Ni-65% Cu. The cleanliness of the surface was also monitored by AES, while the order of the surface was subsequently checked by low energy electron diffraction.

The TDS spectra of adsorbed CO from the alloy showed two peaks associated with binding to Cu and Ni sites, and additional structure related to binding at mixed sites. The CO adsorbs as a molecule and the spectra are characteristic of first order kinetics. Comparing the TDS spectra from surfaces of different composition, it was found that the activation energy of desorption from a Ni binding site decreased linearly with increased surface Cu concentration. (By Ni binding site it is meant that all the metal atoms immediately adjacent to the CO are Ni atoms). This indicates that atoms further away from the gas molecule have a significant effect on the properties of the bond between the CO gas molecule and the metal surface. This is opposed to many current theories of chemisorption which tend to neglect the effect of all but the adjacent metal atoms. We have called this longer range electronic interaction a "ligand effect".

The studies of  $H_2$  chemisorption provide a remarkable contrast. Hydrogen adsorbs dissociatively so the TDS spectra are all characteristic of second order kinetics. As compared to data obtained elsewhere on clean Ni, the TDS spectra from the various alloy surfaces show no additional structure. Furthermore, focusing on the site occupied at low coverages, it was found that the activation energy for desorption remained constant over a wide range of surface composition. It seems that for  $H_2$  adsorption the Cu atoms play a much smaller role in determining the bond between gas molecule and metal surface.

Experiments planned and in progress utilizing a full range of spectroscopic techniques (1) will relate changes in the UPS spectra to the filling of successive adsorption sites and thus hopefully shed light on changes in surface electronic structure, (2) examine more carefully the concentration of Cu and Ni atoms as a function of depth into the bulk and the effect (if any) of different bulk compositions, and (3) study further chemisorption systems and elementary reactions on the surface.

## (2) Studies of Tungsten Carbide as a Substitute for Pt Catalysts

D. T. Ling, K. Y. Yu, J. N. Miller,  
I. Lindau, P. A. Pianetta

(This work is part of a "Thrust" Program on Alloy Catalytic Materials supported by the National Science Foundation's Materials Research Laboratory Program through the Center for Materials Research.)

It has been reported by Boudart and coworkers that the material WC exhibits some catalytic properties similar to those of Pt. A joint program between our laboratory, Prof. Boudart's laboratory, and CMR is currently underway and directed at understanding why WC shares some of the properties unique to Pt and a very few other transition metals, whereas W does not. The development of a practical WC catalyst is a long-range objective. Partially for this reason, Pt is being investigated, details appear in the following report.

Earlier W was studied using ultraviolet photoelectron spectroscopy (UPS) with synchrotron radiation as a light source. These studies were performed at the Stanford Synchrotron Radiation Project (SSRP). Valence band UPS spectra were obtained from the clean W(100) single crystal surface and from the same surface with adsorbed  $O_2$  and  $C_2H_2$ . A carburized surface obtained by heating a  $C_2H_2$  covered surface to

1175° C was also studied. A sharp, very angularly sensitive peak was observed  $\sim 1$  eV below  $E_F$  in spectra of the carburized surface. This led to the assumption that a highly ordered surface layer was present. Later work examining the fine structure of the C Auger peak in AES revealed that in fact a surface carbide had formed.

The W 4f and 5p core levels were also studied. UPS spectra as a function of photon energy provided information as to the changes in photoionization cross section as a function of  $h\nu$ . More importantly, it was of interest to see whether or not chemical shifts of the core levels could be detected upon adsorption of  $O_2$  or the formation of a carburized layer. The adsorption of  $O_2$  resulted only in a broadening of the levels, while the formation of the carbide layer resulted in negligible changes to the core levels.

Further adsorption experiments are planned on W using UPS and TDS combined with the other surface science techniques. Similar experiments will be performed on WC.

### (3) Studies of Pt with Regard to its Special Properties

D. M. Collins

The impetus behind our studies of Pt lies in the rather unique ability of Pt to catalyze a number of industrially important reactions. Our experiments have focused on the adsorption of oxygen and carbon monoxide on Pt and the reduction of adsorbed oxygen by exposure to hydrogen, resulting in the formation of water. The study of  $O_2$  and CO adsorption and the water reaction serves two purposes: first, from a practical viewpoint, Pt is a rather unique catalyst for oxidation reactions such as  $H_2 + 1/2 O_2 \rightarrow H_2O$  (which is important in fuel cells) and  $CO + 1/2 O_2 \rightarrow CO_2$  (which is important in catalytic converters in automobiles), and second, simple systems such as these aid in the development of Ultraviolet Photoelectron Spectroscopy (UPS) as a tool to study the details of the adsorption of the reacting species and the reaction mechanism which could lead to a good enough understanding of the active adsorption states and the reaction mechanism to permit engineering of better and less expensive catalysts to replace Pt in many applications. One such possibility is tungsten carbide which will be



discussed in a later section.

Last year we reported the use of UPS, Thermal Desorption Mass Spectroscopy (TDMS) and Auger Electron Spectroscopy (AES) to study several aspects of catalysis by Pt. We determined that the active adsorption state for oxygen on Pt was a tightly bound atomic state ( $\sim 80$  kcal/mole) with a chemisorptive bond which appeared to be rather delocalized. By using UPS to monitor the progression of the water reaction we were able to propose a mechanism for the reaction, and, based on that mechanism, suggest that the active state of hydrogen on the Pt was a lightly bound molecular state.

The work reported last year, which described the development of UPS as a tool to study catalysis, was performed on polycrystalline Pt foils, which, during the cleaning procedure, had reconstructed such that the individual grains were predominantly oriented with their (111) faces parallel to the surface of the foil. This year we have applied the techniques developed on the polycrystalline surfaces to several single crystal surfaces; namely the (111), 6(111) X (111), and 6(111) X (100) surfaces. The 6(111) X (111) and 6(111) X (100) surfaces are "stepped" surfaces, cut approximately  $10^\circ$  off the (111) direction toward the (110) and (100) directions, respectively. This gives rise to surfaces which are "stepped", i.e., they have terraces six atoms wide and steps one atom high.

The two stepped surfaces showed much the same behavior as was observed on the polycrystalline foil. However, oxygen would not adsorb, except in very small quantities, on the (111) surface. This suggests that the presence of steps (or grain boundaries in the case of the polycrystalline foil) is necessary for the dissociation of the  $O_2$  molecule in order that it adsorb on the Pt surface. This is a critical result since the oxygen chemisorption seems the key step in  $H_2O$  formation.

Further evidence for a difference in the adsorption properties of steps was obtained in the TDMS studies of CO on the single crystal surfaces. On the stepped surfaces two adsorption states were observed, one with a desorption peak temperature of  $\sim 250^\circ C$  and one with a desorption peak temperature of  $\sim 150^\circ C$ . On the (111) surface, however, only a state with a desorption peak temperature of  $\sim 150^\circ C$ . was observed.

The higher temperature desorption states present on the stepped surfaces had  $\sim 1/5$  the occupancy of the lower temperature states as determined by the relative areas under the respective peaks in the TDMS data. This is strong evidence that the higher temperature desorption peaks are associated with adsorption at the steps.

The UPS data also showed interesting behavior, which, at this state in our experiments, appears to be related to the step density. The work function decreased upon CO adsorption in the low coverage region (which we believe corresponds to adsorption at the steps) and then increased in the high coverage region (corresponding to adsorption on the terraces). We have also seen two adsorption states in the TDMS data for hydrogen adsorption on the 6(111) X (100) surface. These measurements were made possible by the addition of the apparatus necessary to cool the Pt to  $\sim -90^\circ \text{C}$ , which is below the desorption temperature of  $\text{H}_2$  ( $\sim 25^\circ \text{C}$ ). The change in work function resulting from hydrogen adsorption followed the opposite pattern to that of CO. First the work function increased, then it decreased. In hopes of conclusively identifying the high temperature desorption peaks and the behavior of the work function changes with the steps, our future plans include the study of two more stepped surfaces: the 12(111) X (111) surface, with half the step density of the 6(111) X (111) and 6(111) X (100) surfaces, and the (110) surface (which can be written in stepped notation as 2(111) X (111)) with three times the step density of the 6(111) X (111) and 6(111) X (100) surfaces.

This work has already given considerable insight into  $\text{H}_2\text{O}$  formation on Pt and has led to the suggestion of a modified model for that reaction involving the reaction of chemisorbed oxygen atoms (formed by steps on surface) and lightly absorbed  $\text{H}_2$  molecules. These results provide a good platform to study the performance of other materials which may serve as substitutes for Pt.

(4) Studies of the Surface and Surface Chemistry of GaAs and Other 3-5 Semiconductors

P.E.Gregory, P.W.Chye, I. Lindau, P.A.Pianetta, and C.M.Garner

The photoemission study of the GaAs surface during the past year concentrated on the clean surface and oxidation of the clean surface. Almost all the GaAs work was performed at the Stanford Synchrotron Radiation Project (SSRP), where light of wavelengths from the visible to soft X-rays is available (photon energies up to 300 eV) for photoemission.

GaAs (110) surfaces were prepared for study by cleaving single crystals in ultrahigh vacuum ( $\leq 10^{-10}$  Torr). Oxygen exposures were made by leaking highly pure oxygen into the vacuum system. Except as noted below, no hot filament ion gauges were used in the main sample chamber during the experiment. Photoemission energy distribution curves (EDCs) were measured using a cylindrical mirror analyzer and electron counting techniques.

Perhaps the most important finding was the verification of our earlier suggestion that for room temperature oxidation, oxygen binds preferentially to the surface As atoms. This fact was demonstrated by photoemission measurements in the energy range  $32 \text{ eV} < h\nu < 300 \text{ eV}$ , where peaks due to the Ga 3-d core levels (19.7 eV below the Fermi level,  $E_F$ ) and As 3-d core levels (41.5 eV below  $E_F$ ) are clearly seen. As the surface is exposed to oxygen, a second peak develops 2.9 eV below the As 3d peak and grows with increasing oxygen exposure. The new peak is equal in height to the original As 3d peak after an oxygen exposure of one atmosphere for 15 minutes, when measured at a photon energy of 100 eV. No new peak develops near the Ga 3d core level. The peak 2.9 eV below the As 3-d core is a chemically shifted peak. The chemical shift is caused by valence electrons moving from the As atoms at the surface to the oxygen atoms which have bonded to the As atoms. The rearrangement of valence electrons changes the potential on the surface As atoms, causing the core levels to shift. The fact that the As core levels show a clear chemical shift, while the Ga core levels do not is very convincing evidence that oxygen bonds preferentially to the surface As atoms during room temperature oxidation.

Chemical shifts such as these discussed above are routinely measured using the X-ray photoemission technique called ESCA. The difference between ESCA and the technique discussed here is that ESCA uses photon energies above 1 keV and is thus most sensitive to the chemistry of the bulk of the material, while we used photon energies  $32 \text{ eV} < h\nu < 300 \text{ eV}$ , which make our results very surface sensitive. A measure of the surface sensitivity can be obtained by comparing the ratio of the area under the chemically shifted As-3d peak (from oxidized As at the surface) to the area under the unshifted As-3d peak (from As atoms within the bulk GaAs) for different photon energies. The relative magnitude of the shifted peak is greatest for  $h\nu \approx 100 \text{ eV}$ , showing that the surface sensitivity is greatest for emission from As 3d levels in GaAs at  $h\nu \approx 100 \text{ eV}$ .

A different surface oxidation takes place when the GaAs is exposed to excited  $\text{O}_2$  created when a hot filament ion vacuum gauge or other source of excitation is running in the chamber. The differences seen from the results discussed above are:

- 1) The oxidation proceeds faster; about 2 orders of magnitude lower exposures with the gauge on are needed to produce equivalent effects to exposures with the gauge off.
- 2) Two chemically shifted As 3-d peaks develop, are 2.9 eV below the unshifted peak, as before, and are 4.5 eV below the unshifted peak. The 4.5 eV peak grows faster than the 2.9 eV peak. The 4.5 eV peak has tentatively been identified as arising from  $\text{As}_2\text{O}_5$ , at the surface.
- 3) A chemically shifted Ga 3-d core peak grows 1 eV below the unshifted Ga 3d core.

These results indicate that, when a hot filament gauge "activates" the oxygen in some way, Ga at the surface is also oxidized. Since theoretical work and chemical valency arguments indicate that the three Ga valence electrons are tied up in covalent bonds to As atoms at the surface, the oxidation of surface Ga atoms can only proceed by breaking covalent bonds at the surface. It has not yet been determined if the "activated" oxygen represents atomic oxygen, ionized oxygen, or an excited state of molecular oxygen.

Photoemission measurements were made in the photon energy range  $7 \leq h\nu \leq 30$  eV from both clean and oxygen exposed GaAs. In this energy range, particular attention was paid to band bending measurements, obtained by measuring the position of the Fermi level relative to the bands at the surface. The Fermi level position is obtained using photoemission measurements from a gold sample, and the position of the bands at the surface is obtained from photoemission measurements from the GaAs.

The primary result from this work was a modification of our earlier model for the distribution in energy of surface states on the (110) GaAs surface. Our new results confirm our earlier finding that there are no filled surface states in the bandgap. We had earlier inferred the existence of a band of empty surface states in the upper half of the bandgap from the fact that the Fermi level was found to be pinned at the middle of the bandgap on n-type GaAs, producing upward band-bending at the surface. Further measurements made at SSRP this last year show that the Fermi level pinning is not present on every sample, and the pinning position on those samples for which pinning is observed is more variable than previously observed. These observations lead us to believe that the pinning is probably not caused by intrinsic surface states, but rather is caused by extrinsic surface states, that is, to states caused by external factors such as cleavage steps or strain or some such factor. The results then indicate that there are no intrinsic surface states within the bandgap.

The shape of EDCs was somewhat more variable than was expected based on our previous photoemission work with conventional UV light sources for  $h\nu < 12$  eV. The relative amplitude of peaks in the EDCs varied from sample to sample, possibly indicating effects due to different orientation of the samples with respect to the highly polarized beam from SSRP, and possible effects due to small changes in acceptance angle of measured photoemitted electrons.

The sharpness of peaks in the EDCs varied from cleave to cleave on the same sample. A remarkable effect is that small oxygen exposures cause the less sharp EDCs to become sharper. Oxygen exposures so small that only  $10^{-3}$  monolayer or less of oxygen could have adsorbed produces a marked sharpening of the EDCs. The oxygen appears to exert a long

range effect, possibly by triggering a rearrangement of the surface atoms.

All of the GaAs work thus far has been on the (110) cleavage face. In the immediate future work will begin on other crystal faces, prepared by heat cleaning and Argon sputter cleaning. Another future area of work will be to study GaAs core level shifts produced by adsorbates other than oxygen. Cesium adsorption on GaAs will be studied in this way because of the technological importance of the III-V negative electron affinity photocathode, which consists of a cesium oxide layer on GaAs or other III-V materials.

(5) Studies of the Surface and Surface Chemistry of GaSb and InP

P.W.Chye, P.E.Gregory, I.Lindau, P.A.Pianetta and C.M.Garner

The GSCH (Gregory, Spicer, Ciraci and Harrison) model for the (110) surfaces of the group III-V semiconductors, described in last year's report, has been further supported during the past year by experiments performed here and at other research laboratories. This model associates the empty surface states with the column III surface atoms and the filled surface states with the column V surface atoms, with a bandgap of considerable size separating the two.

Detailed studies on the (110) cleavage faces of InP and GaSb indicate that the Fermi level ( $E_F$ ) is pinned on n-InP at 0.25 eV below the conduction band minimum (CBM) and is unpinned on n- and p-GaSb. Studies made at SSRP using synchrotron radiation show that  $E_F$  is unpinned on p-InP. In no case is emission from filled surface states observed. The pinning on n-InP may be due to empty intrinsic surface states or other states extrinsic in nature. Since  $E_F$  can be pinned by less than  $10^{12}$  states/cm<sup>2</sup>, a small number of extrinsic states due to defects or surface strain can cause pinning. The Cs-Schottky barrier pinning position is very close to the pinning position on the clean surface InP, but no correlation with empty intrinsic surface states can be made as it is not clear what is actually causing the pinning on the clean surface. In InP, as in GaAs, the high energy edge of the valence band emission is seen to move to higher energy into the bulk bandgap as Cs coverage is increased to near one monolayer, indicating a very strong interaction between the Cs and the InP surface. Oxidation

of n-type InP produced very little  $E_F$  movement, whereas the p-type sample studied at SSRP exhibited a high sensitivity of  $E_F$  to oxygen.  $E_F$  on p-InP starts to move up towards the CBM at 1 Langmuir ( $1L = 10^{-6}$  Torr sec) of oxygen exposure and by  $10^7L$  has moved by more than 0.6 eV to near midgap.

Very interesting and exciting results have been obtained on GaSb. As mentioned above,  $E_F$  is unpinned on the clean surface, so that there are no surface states - intrinsic or extrinsic - in the bandgap. Upon application of Cs to n-GaSb,  $E_F$  starts moving through most of the bandgap, from near the CBM to near the valence band maximum (VBM). This shows directly for the first time that Schottky barrier pinning on a III-V material is not produced by intrinsic surface states characteristic of the clean surface (as suggested by Bardeen, Mead and others) but rather is produced by states induced by the metal placed on the semiconductor. The same striking movement downward of  $E_F$  is also seen when n-GaSb is oxidized. By  $10^5L$  exposure  $E_F$  has moved downward in energy by 0.55 eV and with further oxidation moves back upward by a small amount of about 0.2 eV.

The surface chemistry of GaSb is quite different from that of GaAs or InP. Cs does not adhere as tightly to the surface of GaSb as to those of the other two, and to produce the lowest electron affinity on this material a thicker layer of Cs is required, which is not very stable and partially desorbs immediately. When oxygen is applied to Cs covered GaSb, EDCs taken reveal structure characteristic of bulk Cs-oxide whereas numerous cycles of Cs-oxygen treatment is necessary before similar structure is observed on GaAs. The large differences in surface chemistry is very probably due to different rearrangement within the surface unit mesh as the crystals are cleaved.

When "unexcited" oxygen (see preceding section) is applied to GaSb, it tears up the lattice at once forming both  $O_2$  and Sb oxides. This is in contrast to GaAs where such exposure does not tear up the lattice but only forms oxygen bonded to the As "dangling bonds".

#### (6) Studies of the Oxidation of Si and Ge

C.M.Garner, P.A.Pianetta, I.Lindau and J.N.Miller

In recent years, passivation of semiconductor surfaces has be-

come extremely important especially in relation to MOS technology. Since Si is the major semiconductor material used in MOS technology it is very important to understand the basic physics of the connective region between the Si and SiO<sub>2</sub>. In order to improve the understanding of the surface states and oxidation processes in Si and Ge, photoemission studies of these materials has been made at SSRP. By selecting the most surface sensitive photon energy for looking at the valence band and the Si 2p level or Ge 3d level it is possible to carefully monitor the changes in the valence and chemical shifts of the appropriate core levels associated with different states of oxidation of the surface atoms.

Studies of the photoemission of cleaned Si indicate that there is a filled surface state extending into the bandgap. It was also found upon one cleave that another surface state existed superimposed upon the first state. This surface state is associated with a surface state arising from a high step density on the cleavage plane. Upon exposure to O<sub>2</sub> it was found that the second surface state disappeared more rapidly than the first surface state. This indicates that the surface state located at the steps may be more chemically active than the other surface states.

Upon exposure to oxygen, in general, the filled surface state disappeared quite rapidly with exposure of O<sub>2</sub> up to 10<sup>3</sup>L O<sub>2</sub>, while the number of Si atoms bonded to the oxygen did not increase as rapidly or linearly. This indicates that the disappearance of the filled surface state may be associated with a reconstruction of the surface with less than every Si atom being bonded to oxygen.

It has generally been thought that monolayer coverage of O<sub>2</sub> is obtained with 10<sup>3</sup>L O<sub>2</sub> exposure to O<sub>2</sub>; however, the studies of bonding coverage by observing the number of bonded Si atoms increases by a factor of approximately two between exposures 10<sup>3</sup> and 10<sup>7</sup>L O<sub>2</sub> with no indication that oxygen was penetrating beneath the surface of the Si. This indicates that the definition of monolayer coverage of O<sub>2</sub> may be questionable and that only one half monolayer coverage may exist at 10<sup>3</sup>L O<sub>2</sub> with monolayer coverage existing at 10<sup>7</sup>L O<sub>2</sub>.



At exposures above  $10^7 \text{ L O}_2$  it was observed that the Si 2p core level had a component which had a larger chemical shift than observed at lower exposures. This indicates a more stable bonding configuration which can be associated with the oxygen breaking beneath the surface and bonding to more than one Si with the O atom between 2 Si atoms and the silicon atoms having more than one oxygen nearest neighbor. At very heavy oxygen exposure the Si 2p core level was found to be shifted almost to the  $\text{SiO}_2$  oxidation state, although there was also approximately one layer still forming the connective region. Thus the connective region appears to proceed before the oxide region in the growth process.

In the Germanium, similar results were obtained by observing the shifting of the Ge 3d level and the valence band.

#### (7) Synchrotron Radiation Studies of Metals

I. Lindau, P. A. Pianetta and K. Y. Yu

We continued our investigation of metals using synchrotron radiation by performing extensive studies on gold and copper. Our work represents the first photoemission measurements performed on either of these materials above 100 eV (and below 1000 eV).

In gold, we have studied the partial photoionization cross sections of the valence bands as well as for the 4f levels (binding energy 84 eV) up to about  $\hbar\omega = 300$  eV. This is a very interesting energy range in which to study the 4f levels because we are able to observe the cross sectional behavior at and just above threshold. It is in this region that large variations in cross section take place. These are the first such measurements that have been done and they compare favorably to calculations by other workers.

We have also observed a very interesting energy dependence in the valence band of gold between  $\hbar\omega = 80$  and 200 eV. The gold valence band for  $\hbar\omega = 80$  eV looks very much like the XPS spectrum (at 1486.7 eV) and the calculated one-electron density of states. However, between 100 and 200 eV, the valence band structure is slowly modulated and the relative amplitudes of the two valence band peaks are reversed. At  $\hbar\omega = 180$  eV, the valence band again has about the same shape as at 80 eV. This illustrates the importance of cross sectional effects in determining the total shape of the distribution curves.

The main surprise we encountered when we performed photoemission measurements for the first time above 100 eV on copper was the relatively low cross section of the 3p levels (binding energy 76 eV) compared to the 3d levels (valence band). From XPS measurements ( $\hbar\omega = 1486.7$  eV) it is well known that the cross section of the 3p levels is about four times that of the 3d's. Thus, it is apparent that the relative cross section for 3p and 3d electrons changes very drastically between  $\hbar\omega = 100$ -200 and 1500 eV, and that the cross section of the 3p electrons has a very slow onset from threshold upward.

#### (8) Auger Analysis of $\text{SiO}_x$ and the Si-SiO<sub>2</sub> Interface

J. S. Johannessen

Auger Electron Spectroscopy (AES) has been applied to a study of the chemical and physical properties of evaporated layers of  $\text{SiO}_x$ , where  $1 < x < 2$ . In this study we discovered for the first time the chemical shift in the KLL Auger transitions in Si. This discovery led us to the conclusion that evaporated  $\text{SiO}_x$  films are phase separated in the sense that, for  $1 < x < 2$ , silicon exists as microscopic inclusions in a matrix of amorphous  $\text{SiO}_2$ . Our results have resolved a long standing controversy regarding the microscopic structural properties of  $\text{SiO}_x$  films. One school of thought regarding the  $\text{SiO}_x$  matrix as homogeneous and randomly bonded, while the other school of thought viewed  $\text{SiO}_x$  as a microscopic mixture of Si and  $\text{SiO}_2$ . This work was necessary in order to properly evaluate the results from our studies of the MOS structures.

Using AES in conjunction with simultaneous argon ion sputtering we have studied the chemical and physical structure of the interface region between the silicon substrate and the layer of silicon dioxide formed by thermal oxidation of the substrate. Here we have made use of the ability to distinguish between the different chemical states of silicon to show that the  $\text{SiO}_2$ -Si interface is phase separated over 20 to 30 Å in the direction perpendicular to the interfacial plane. We believe that the interface region consists of a natural roughness which is formed as a result of the growth process of the oxide. Interfacial strain and the net influx of oxygen at the interface are among the

major contributing factors to the morphology of this interface. Our observations and our interpretations have given rise to questions and debate about the relation between the morphology and the electronic properties of this very important interface. However, continued investigations and new research tools are needed to completely resolve the controversy of the debate. We believe that AES and ion sputtering is one of the more useful techniques in this respect.

Recently we have studied pile-up of phosphorus in the silicon substrate at the  $\text{SiO}_2$ -Si interface as a result of thermal oxidation. Preliminary interpretation of the pile-up effect indicates that the redistribution of phosphorus is not as effective as previous electronic measurements suggested. A more complete study will be published at a later stage.

Silicon nitride is also important to the electronic industry as a diffusion barrier and as an integral part of MNOS electronic memory devices (MNOS = Metal-Nitride-Oxide-Silicon).

The properties of silicon nitride are not as well known as that of  $\text{SiO}_x$  or  $\text{SiO}_2$ . AES analysis carried out by us has shown that Chemically-Vapor-Deposited (CVD) nitrides are rich in silicon. This means they should behave similarly to  $\text{SiO}_x$ , where  $x \lesssim 2$ . Our results indicate that this is generally the case. A report on this subject will be issued in the near future.

The work reported here signifies new advances in the Auger-sputter technique and indicates results important to applications in integrated circuit components; however, these new techniques should have increasingly important applications in the metallurgical as well as electronics industry. Above all the work shows a very successful collaboration between an industrial concern, Varian, and Stanford.

(9) Characterization of Fly Ash and Related Oxides using Auger Spectroscopy.

R. A. Powell

Fly ash produced from the combustion of coal is a complex mixture of microscopic metal oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,

etc.) that range in size from a few hundred microns to a fraction of a micron. It is extremely difficult to measure the chemical composition of individual fly ash particles using conventional chemical analysis. Yet it has long been recognized that the chemical composition of the individual particles, particularly their surface composition, is of great importance in determining their electrical and physical properties and their detrimental health effects when they are emitted into the atmosphere.

We have originated and are presently carrying out a research program to investigate the surface and bulk composition of fly ash and closely related metal oxides using Auger electron spectroscopy (AES) in conjunction with ion-milling as the primary technique. Using this technique the chemical composition of an individual fly ash particle can be measured as a function of depth into the particle. This is accomplished by bombarding the ash surface with energetic ions (energy 1-3 keV) of a noble, unreactive gas such as Argon. As layers of the ash are continuously sputtered away by the ion beam, AES is used to monitor the elements present at the surface of the sample, their chemical state and abundance. By increasing the spot size of the primary electron beam used in the AES analysis, an average over many thousands of the microscopic particles can also be obtained. In the several fly ash samples we have studied to date (collected electrostatically from the flue gas of commercial coal-fired electric power plants), significant changes in composition have been observed within several hundred Angstroms of the surface.

We are also using AES to investigate the chemical state of elements present in the ash. For example, in  $\text{Na}_2\text{S}_2\text{O}_3$ , sulfur is known to exist equally in two different oxidation states, +6 and -2. In the AES spectrum of this substance we have observed two Auger peaks associated with the LMM Auger transition in sulfur separated by about 5 eV. If the sulfur were present in only one oxidation state, only one peak would have been observed. Careful AES measurements of the sulfur peaks in fly ash are underway and could reveal if this element is present as free sulfur, combined as a sulfate or sulfite, bound to the ash surface as  $\text{SO}_2$ , etc. Such information is important as inhalation of sulfur

from fly ash may be a serious health hazard.

Quantitative data on bulk and surface composition obtained with AES is being compared with results obtained by other diagnostic techniques including emission spectroscopy and electron microprobe analysis.

The most widely used method of removing particulate matter from smokestack gases is the electrostatic precipitator. A common cause of poor precipitator performance is associated with a high DC resistivity of the ash being collected ( $> 10^{11}$  Ohm-cm), a condition found following the combustion of most low-sulfur Western coals. Therefore, in addition to the AES measurements, we will be determining DC resistivity for the ash samples. Our goal in this part of the research is to understand the way in which surface and bulk composition affect the electrical conduction in the ash.

#### (10) Investigation of Tin Oxide and Related Oxides with Regard to Cold Cathodes

R. A. Powell

As first reported by Russian workers, tin oxide films have shown promise as cold electron emitters, i.e., cold cathodes. Our objective has been to try to better understand the mechanism of emission in these cold cathodes and in related oxides which may exhibit similar phenomena. To this end we have carried out UV photoemission (UPS) and Auger electron spectroscopy (AES) measurements on  $\text{SnO}_2$  films and related oxides. Particularly noteworthy has been the recent report that strong electron emission can be obtained from sputtered films of indium-tin-oxide ( $\text{In}_2\text{O}_3\text{-SnO}_2$ ). After an initial forming process, or activation, emission currents in excess of 1.5 mA are obtained with efficiencies of about 10% for such films. Since this emission current is an order of magnitude larger than for  $\text{SnO}_2$  we are currently directing our attention to the indium-tin-oxygen system. We are presently fabricating  $\text{In}_2\text{O}_3\text{-SnO}_2$  samples, activating them and measuring their emission characteristics (e.g., emission current as a function of film voltage, film current, anode voltage and spacing; energy spread of the emitted electrons, etc.). AES and UPS are then used to correlate the measured performance of the emitters with any detectable changes which may have occurred in the surface

composition or electronic structure of the films following activation. This data is presently being collected and analyzed.

(11) The Oxidation of Aluminum

J. N. Miller, K. Y. Yu, and P. W. Chye

The study of the oxidation of Al came of interest due to recent theoretical calculations of electronic structure of the oxygen-Al interface. Lang and Williams studied the electronic structure of an oxygen atom chemisorbed on a jellium metal of a density roughly that of Al.

The experiment was performed by evaporating Al from an electron gun onto a niobium single crystal. Because of the high chemical reactivity of Al, it was difficult to prepare and prolonged outgassing was necessary to obtain a clean film. The photoemission was performed on a He resonance lamp for  $h\nu = 21.2$  eV on a McPherson monochromator with a hydrogen discharge lamp for  $h\nu < 11.8$  eV. The clean EDC at 21.2 is characterized by a high scattering peak which decreases monotonically to the Fermi edge (Al is almost transparent to 21.2 eV). Small exposures to oxygen cause a broad resonance band to form 7.2 eV below  $E_F$  ( $\sim 3$  eV FWHM) and negligible work function change. At higher exposures, a second peak appears 13.5 eV below  $E_F$ . We interpret this to mean that at low exposures the oxygen dissociates and penetrates the surface. This is born out in the high heat of formation and by comparison to such metals as Sr and Cs.

These results were in disagreement with those of Lang and Williams. They have since changed their calculation to allow the oxygen atom to move into the Al surface. When the oxygen atom is just inside the surface, they find that the energy position of the oxygen Al state is in better agreement with our experimental findings.

## PUBLICATIONS

Photoelectron Spectra of Condensed Gases on an Inert Substrate, K.Y. Yu, J.C. McMenamin and W.E. Spicer, J. Vac. Sci. Technol. 12, 286 (1975).

Direct Observation of Anion Formation in the Electronic Structure of Tetracyanoquinodimethane (TCNQ) Charge-Transfer Salts, B.H. Schechtman, S.F. Lin and W.E. Spicer, Phys. Rev. Letts. 34, 667 (1975).

DOD Sponsored Research, W.E. Spicer, Letter to Editor, Science, 188, 678 (1975).

Optical Properties of CsI(Na) and Heat-Treated Pure CsI, C.W. Bates, Jr., O.L. Hsu, A. Salau and W.E. Spicer, Physics Letters, 51A, 425 (1975).

UPS Measurements of Molecular Energy Level of Condensed Gases, K.Y. Yu, J.C. McMenamin and W.E. Spicer, Surf. Sci. 50, 149 (1975).

The Oxidation of Cs UV Photoemission Studies, P.E. Gregory, P. Chye, H. Sunami and W.E. Spicer, J. Appl. Phys. 46, 3525 (1975).

Use of Photoemission, Auger, and Thermal-Desorption Techniques to Study the Mechanism of a Catalytic Reaction, D.M. Collins, J.B. Lee and W.E. Spicer, Phys. Rev. Lett. 35, 592 (1975).

Phase Separation in Silicon Oxides as Seen by Auger Electron Spectroscopy, J.S. Johannessen, W.E. Spicer, Y.E. Strausser, Appl. Phys. Lett. 27, 452 (1975).

Photoemission Studies of the GaAs-Cs Interface, P.E. Gregory and W.E. Spicer, Phys. Rev. B 12, 2370 (1975).

Electron Escape Depth, Surface Composition, and Charge Transfer in Tetra-thiafulvalene Tetracyanoquinodimethane (TTF-TCNQ) and Related Compounds: Photoemission Studies, S.F. Lin, W.E. Spicer, B.H. Schechtman, Phys. Rev. B 12, 4184 (1975).

GaSb Surfaces States and Schottky-Barrier Pinning, P.W. Chye, I.A. Babalola, T. Sukegawa, W.E. Spicer, Comments-Phys. Rev. Lett. 35, 1600 (1975).

Photoemission Study of the Formation of Schottky Barriers, W.E. Spicer, P.E. Gregory, P.W. Chye, I.A. Babalola and T. Sukegawa, Appl. Phys. Lett. 27, 617 (1975).

Further Evidence for Equilibrium Surface Segregation in the Cu-Ni Alloys-CO and H<sub>2</sub> Chemisorption, C.R. Helms, K.Y. Yu and W.E. Spicer, Surf. Sci. 52, 217 (1975).

Determination of the Oxygen Binding Site on GaAs (110) Using Soft X-Ray Photoemission Spectroscopy, P. Pianetta, I. Lindau, C. Garner and W.E. Spicer, Phys. Rev. Lett. 35, 1356 (1975).

The Intrinsic Linewidth of the 4f Levels in Gold as Determined by Photoemission, I. Lindau, P. Pianetta, K. Yu, and W.E. Spicer, Phys. Lett. 54A, 47 (1975).

Negative Affinity Photocathode Research and Technology, W.E. Spicer, IEDM Digest 4.1, 57 (1975).

Synchrotron Radiation as a New Tool Within Photon-Beam Technology, S. Doniach, I. Lindau, W.E. Spicer, and H. Winick, J. Vac. Sci. Technol. 12, 1123 (1975).

Bulk and Surface Ultraviolet Photoemission Spectroscopy, W.E. Spicer, Chapter 12 in Optical Properties of Solids-New Developments, Edited by B.O. Seraphin, pp. 631-676, North Holland Publishing Co., Amsterdam (1976).

Photoemission Study of Surface States of the (110) GaAs Surface, P.E. Gregory and W.E. Spicer, Phys. Rev. B 13, 725 (1976).

Photoemission of Gold in the Energy Range 30-300 eV Using Synchrotron Radiation, I. Lindau, P. Pianetta, K.Y. Yu and W.E. Spicer, Phys. Rev. B 13, 492 (1976).

Ultraviolet Photoemission Study of Cesium Oxide Films on GaAs, P.E. Gregory and W. E. Spicer, J. Appl. Phys. 47, 510 (1976).

Photoemission Studies of Surface and Interface States on III-V Compounds, W.E. Spicer, P.W. Chye, P.E. Gregory, T. Sukegawa and I.A. Babalola, J. Vac. Sci. Technol., 13, 233 (1976).

Study of the Hydrogenation of O Adsorbed on Pt, D.M. Collins, J.B. Lee and W.E. Spicer, J. Vac. Sci. Technol. 13, 266 (1976).

Photoemission from Some Metals and Semiconductors in the Energy Range 5-350 eV, I. Lindau, P. Pianetta, K.Y. Yu and W.E. Spicer, J. Vac. Sci. Technol. 13, 269 (1976).

Relationship of Heat of Chemisorption to  $\pi$ - and  $\sigma$ - Level Shifts as Measured by Photoemission, K.Y. Yu, W.E. Spicer, I. Lindau, P. Pianetta and S.F. Lin, J. Vac. Sci. Technol., 13, 277 (1976).

Photoemission Study of the Adsorption of O<sub>2</sub>, CO and H<sub>2</sub> on GaAs (110), P.E. Gregory and W.E. Spicer, Surf. Sci. 54, 229 (1976).

Photoemission Investigation of Surface States on Strontium Titanate, R.A. Powell and W.E. Spicer, Phys. Rev. B 13, 2601 (1976).

A Study of the Chemical Composition of MOS and MNOS Structures by Auger Electron Spectroscopy, J.S. Johannessen, W.E. Spicer, Y.E. Strausser, Thin Solid Films, 32, 311 (1976).



#### 64. SOLID STATE PHYSICAL CHEMISTRY

D. A. Stevenson, Professor, Materials Science and Engineering

##### Professional Associates:

A. G. Elliot  
B. L. Mattes

##### Graduate Students:

H. Dun	F. Q. Johnson*
S. Hahn	E. D. Jones
Z. S. Jan	S. M. Liu

\*Received MS during report period.

##### Agency Support:

NSF through CMR  
ERDA AT(04-3) 326 PA-37  
Office of Naval Research - N00014-67-A-0112-0082  
National Science Foundation-RANN-NSF AER 74-13036  
NSF/MRL through CMR - Thrust Program on Synthesis, Characteri-  
zation and Properties of Noncrystalline Metallic Alloys

#### (1) Diffusion of Oxygen in Liquid Metal Systems

##### Objective and Approach:

This research program concerns the diffusion of oxygen in liquid metals and alloys at elevated temperatures using electrochemical techniques employing solid oxide electrolytes. Emphasis is placed on metal-oxygen systems of technological interest as well as on systems whose study offers the greatest promise of improving our understanding of diffusion processes in liquid metals. There is particular emphasis on metals which form relatively stable oxides, hence, it is necessary to study these systems in a regime of low oxygen pressure. The metal alloy system gallium-indium is selected for initial study.

The experimental approach utilizes the potentiostatic technique with the oxygen concentration cells: liquid metal-oxygen electrode/solid oxide electrolyte/reference oxygen electrode. A step jump in applied potential is reflected as a new surface concentration of oxygen at liquid metal-oxygen electrode surface and a flow of current through the cell establishes a new equilibrium concentration in the liquid metal

electrode with the rate of attainment related to the diffusion coefficient of oxygen in the liquid metal. Appropriate analysis of the current-time relationship allows computation of the diffusion coefficient.

#### Research Report:

The diffusion of oxygen,  $D(O)$ , in the Ga-In-O liquid metal system was measured for temperatures between 750 and 950°C for several Ga-In compositions. Additional experiments, using potentiometric-coulometric titrations, were performed to determine the activity of oxygen as a function of oxygen composition and the saturation solubility of oxygen in pure Ga and In, respectively. It was found that  $D(O)$  versus composition isotherms show three distinct regions, with large changes of  $D(O)$  occurring in the terminal 5 atomic percent Ga and In. The experimentally determined thermodynamic factor did not explain the large changes in  $D(O)$ , however, qualitative correlations with the oxygen solubility and the liquid metal viscosity were observed.

#### (2) Analysis of Dynamic Reacting Systems Using Mass Spectrometric Techniques; Control of Impurities in the Epitaxial Growth of High Quality GaAs

##### Purpose and Objective:

The purpose of this program is to develop techniques for analyzing dynamic high temperature reacting systems using a molecular beam mass spectrometry. The specific system in question is a GaAs liquid phase epitaxial growth system and the associated chemical transport reactions. These reactions involve the protective atmosphere, the reactor walls and the crucible materials and are important sources of contamination during the epitaxial growth process. The present program is directed toward a quantitative study of this phenomena by analyzing the thermodynamics and kinetics of possible transport reactions. The practical relevance of this program is the obvious need to control impurity levels in semiconductors which are used for devices.

Various gas-solid interactions are selected which are relevant to liquid-phase epitaxial growth, for example: fused quartz-graphite-

hydrogen; high purity alumina - boron nitride - argon. The vapor species in these systems will be analyzed with a specially designed sampling probe which forms a molecular beam of a representative sample and introduces it into a quadrupole mass analyzer. The ultimate objective is to identify sources of impurities, determine their influence on the electrical properties of GaAs, and learn how to control them by appropriate modification of the growth procedure.

#### Research Report:

The molecular beam mass analyzer (MBMA) was designed, constructed, and preliminary analysis of its operation was made. The system demonstrated the capability of detecting gaseous species in the parts per million range. Key parts of the apparatus are the sampling orifice, the skimmer orifice and the final columnating orifice which leads to the quadrupole mass analyzer. The three stages are differentially pumped with respective pressures of  $10^{-3}$ ,  $10^{-5}$ , and  $10^{-9}$  Torr. The skimmer orifice is manipulated with respect to the sampling orifice so that different portions of the beam-developed by the expansion through the sampling orifice may be selected by the skimmer. In this manner, the profile of the pressure the size of the Mach disc was established as a function of temperature.

It was confirmed that the beam was operating in the supersonic regime and that the beam is essentially a pure molecular beam. In order to determine the degree of compositional change produced by the expansion through the sampling orifice, the enhancement of the gaseous species is under study.

### (3) Chemical Vapor Deposition of Refractory Compounds of Variable Composition and Particle Size

#### Purpose and Approach

There are three major objectives for this research program:

- (1) to synthesize ultrafine powders of various materials, including nitrides, oxides, carbides, and elemental materials by chemical vapor condensation (CVC) techniques; (2) to characterize the powders; and
- (3) to analyze the synthesis process. The study enhances the fundamental

understanding of the chemical vapor deposition process and also provides a timely input to the current powder synthesis technique.

To achieve the above objectives, systems were designed and constructed to produce powder by homogeneous vapor phase reaction. In addition, systems were developed to remove particles from the gas stream without contamination or further reaction. After suitable trapping, the particles are studied by a combination of techniques: transmission electron microscopy, x-ray and electron diffraction; bulk chemical analysis by neutron activation and electron microprobe analysis; optical analysis; and chemical reactivity.

#### Research Report:

The recent activity on this program has resulted in the development of a versatile CVC reactor for the synthesis of a number of compounds and elements, particularly BN, GaN,  $\text{Al}_x\text{Ga}_{1-x}$ ,  $\text{TiO}_2$ , Zr, and  $\text{Si}_3\text{N}_4$ , with particular emphasis on the synthesis of fine particles. Particles in the 50-1000Å range have been synthesized and isolated and it was found in many cases that the fine particles were amorphous. Two important areas of activity have evolved, namely, the development of techniques for trapping fine particles, and the development of techniques for characterizing the particle size and the structure of fine particles. In the former area, fluid trapping systems have proven to be the most effective. In the latter, transmission electron microscopy has been the most productive tool, however, x-ray techniques and infrared spectroscopy have also provided valuable additional information to characterize the particles.

The characterization of the powder has been seriously hampered by the extreme chemical reactivity of the powders; the small particle size of the material (40-2000Å) made by this process exhibits peculiar properties in terms of physical and chemical reaction, such as agglomeration, sintering and oxidation at room temperature. These difficulties are slowly being overcome by careful handling and specially developed techniques for characterization.

A useful tool that has been developed for analyzing the process is the visual determination of the reaction interface, combined with

mathematical modeling based on models for combustion processes. Much has been learned concerning the basic hydrodynamic and kinetic aspects of the process, even though rigorous solution of the appropriate differential equations is not possible.

#### (4) Vapor Growth and Structural Characterization of Heteroepitaxial Semiconductor Layers

##### Objective:

This program explores the interrelationship between the preparation of thin semiconducting films, their structure, and their electrical properties and device application. The program in progress is specifically directed towards the heteroepitaxial deposition of gallium nitride (GaN) films on sapphire substrates, with particular reference to the preparation of light emitting diodes.

##### Approach:

Gallium nitride layers are grown on sapphire substrates using the vapor phase reaction between gallium monochloride and ammonia, with careful monitoring of the significant growth variables. These films are characterized using a variety of techniques which include: optical microscopy, scanning electron microscopy, and x-ray techniques. There is particular interest in the nature of the semiconducting-insulating (s-i) junctions formed in this material by doping GaN with Mg during growth. This junction structure is used to prepare violet light emitting diodes.

##### Research Report:

Current work has emphasized two major areas: the importance of the catalytic nature of the reactor environment; and the correlation of the doping content with cathodoluminescence.

It was found that the growth environment influenced the extent of  $\text{NH}_3$  decomposition by virtue of relative catalytic potency; in the presence of pure quartz and graphite, there was negligible decomposition of  $\text{NH}_3$ , whereas in the presence of partially decomposed GaN (which produced a Ga-GaN mixture) extensive  $\text{NH}_3$  decomposition occurred.

Substantial differences in the character of the deposited films were noted with differences in the catalytic potency of the reactor environment.

It was found that the CL intensity of a GaN specimen depends on its Mg concentration. As the amount of Mg in the GaN lattice increases to the full compensation level, as indicated by the resistivity change, the overall CL intensity decreases to complete extinction and the spectral maximum shifts to longer wave lengths. These effects are presumably due to the increased density of recombination centers, predominantly non-radiative, generated by the incorporation of Mg deep level impurities. These results established a basis for the characterization of Mg distribution in the GaN crystal. This technique was applied to GaN metal-insulator (GaN:Mg)-n-type semiconductor (GaN) or MIN, electroluminescent diodes in order to determine the non-uniformity of Mg distribution in the insulating layer. Relevant CL micrographs indicate that, in some cases, isolated conducting grains are embedded in an otherwise insulating matrix. This observation was correlated with specific device characteristics to provide a basis for rationalizing device performance.

#### (5) Thin Film Gallium Arsenide for Low Cost Photovoltaic Energy Conversion

##### Purpose and Approach:

The purpose of this program is to develop techniques for growing gallium arsenide (GaAs) thin films on oxide single crystal substrates using liquid phase heteroepitaxial growth methods. Spinel, sapphire, and quartz substrates are under study. The melt temperature, the temperature gradient at the substrate/melt interface, the nature of the substrate surface, and the substrate orientation are the primary parameters under investigation. Nucleation and growth kinetics are correlated with these parameters. The films are analyzed by scanning and transmission electron microscopy, optical microscopy, and van der Pauw measurements.

#### Research Report:

A horizontal quartz reaction chamber and sliding substrate, graphite growth cell have been designed and constructed. Both transient and steady-state growth modes are utilized. Internal heaters are incorporated into the design in order to facilitate achieving high temperature gradients. Initial growths have emphasized the importance of achieving a properly treated substrate surface as well as establishing that difficulties exist in achieving sufficient supersaturation in the liquid to initiate heterogeneous nucleation on the substrate surface. Growth runs in the temperature range 600°C to 900°C have shown that nucleation is favored at higher temperatures.

#### (6) Thermodynamic Stability and Electrochemical Behavior of Amorphous Materials

(Part of Thrust Program on Synthesis, Characterization and Properties of Noncrystalline Metallic Alloys)

##### Purpose and Approach:

The purpose of this program is to quantify the stability of amorphous materials with respect to the stable crystalline phase. This study is of interest in relation to the ease of synthesis of amorphous materials as well as their stability with respect to decomposition to the stable crystalline phase. The approach taken in this study utilizes electrochemical cells employing amorphous materials as one electrode. From standard electrochemical relationships, the electromotive force (EMF) of such cells, when operated close to reversible conditions, may be related to the chemical potential of specific species in the amorphous phase and the temperature coefficient of the cells may be related to the partial molar enthalpy and entropy values. Both aqueous and organic electrolytes are utilized. Major emphasis is placed on the evaluation of the extent of reversibility of these cells. Additional related studies that are also planned concern the dynamics of electrode processes of amorphous materials, specifically, the dynamics of anodic dissolution. These studies have fundamental significance in elucidating the nature of amorphous materials as well as practical value, relating, for example, to the corrosion behavior of these materials.

#### Research Report:

The initial activity has been devoted primarily to two areas: the preparation of samples suitable for electrochemical study; and setting up and evaluating suitable measurement apparatus. In addition, some preliminary cell measurements have been made. The Ag-Cu system was selected for initial study and techniques for the preparation of both amorphous films and metastable crystalline films were developed by Dr. Troy Barbee and his associates at the Center for Materials Research using sputtering as the preparative technique. Preliminary electrochemical measurements were made on a Ag-65%Cu amorphous alloy; however, there was considerable drift in the EMF with time and the final stable values for the EMF indicated an activity coefficient for Cu that was less than unity, contrary to expectations for a metastable or unstable phase. It is believed that the oxide films which commonly form on Cu surfaces may be responsible for this behavior and we are presently establishing special cleaning procedures for the alloys to overcome this difficulty.



## 65. FUNDAMENTAL ASPECTS OF REACTIVITY IN INORGANIC SYSTEMS

H. Taube, Professor of Chemistry

### Professional Associates:

G. Brown	J. Kung
D. Franco	C.P. Wong
A. von Kameke	G. Nord
K. Rieder	

### Graduate Students:

C. A. Stein	J. D. Buhr
S. K. Seidel	J. Sutton
J. P. Sen	D. Walker
H. J. Krentzien	M. Gilberg
M. A. Willis	

### Agency Support:

NIH GM 13638-11  
NIH GM22045-01  
NSF MPS73-04859-A02  
NSF AER75-11204  
PRF8377-ACS

### Technical Objectives:

A. Electron Transfer in Chemical Systems. Apart from the intrinsic interest in understanding what factors govern the direction and mechanism of electron flow between metal centers, the results are important in laying the foundation for understanding one of the major classes of chemical change, those involving oxidation-reduction.

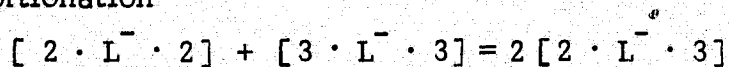
They are relevant also to understanding electronic conduction. In the simplest case, only two centers are dealt with, and the electron transfer process in such an instance can be regarded as an elementary step, subject to systematic study, a study which can help to relate electronic conductance to the fundamental properties of the component atomic centers. Furthermore, the way is open now to proceed by small increments to the study of multicenter systems and to make a systematic study of the transition from the two-center case to those in which electronic conduction as it is ordinarily understood is of interest.

B. Effect of Metal Ions on Reactivity of Ligands. The issue being raised by the heading is of fundamental importance in understanding the role of metal-containing compounds as catalysts. Of special interest to us are Ru(II) (or Os(II)), which can modify the properties of ligands by back bonding. This interaction is lost on oxidation to Ru(III) (or Os(III)), and the changes in reactivity attending oxidation can be studied.

#### Research Report:

##### A. The mixed valence system derived from

$$[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{N}\equiv\text{C}-\overset{\text{R}}{\underset{\text{H}}{\text{C}}}-\text{C}\equiv\text{N}\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+} \quad (\text{I})$$
 by  $1e^-$  oxidation reveals a new kind of electronic interaction between metal ions through conjugated bond systems. On  $1e^-$  oxidation of (I), the pK value for the proton on the middle carbon is decreased by a factor of at least  $10^{12}$  to a value of about 2.0. The mixed valence complex shows the most intense intervalence transition so far recorded for these species ( $> 10^4$ ). The band width and the high value ( $> 10^{10}$ ) of the equilibrium constant for disproportionation



( $[2 \cdot L^- \cdot 2]$  represents 1 with a proton removed from the bridging ligand) speak for valence delocalization in the mixed valence species. In contrast to the cases so far studied which involve  $\pi d$  delocalization into  $\pi^*$  ligand levels, in the present system there is delocalization from a  $\pi$  ligand level,  $\pi$  electrons becoming available on deprotonation, into a  $\pi d$  vacancy on Ru(III). These systems seem to be good prospects for elaborating into linear conductors.

B. Progress has been made in the synthesis of pentaammine-osmium(II) complexes with  $\pi$  acid ligands. As expected such complexes show dramatic effects ascribable to back donation. For example,  $Os(NH_3)_5^{2+}$  increases pK for coordinated pyrazinium ion by almost 7 units; the corresponding effect for  $Ru(NH_3)_5^{2+}$  is only 2 units. Even though  $(NH_3)_5OsOH_2^{2+}$  is too strongly reducing to survive in water,  $[(NH_3)_5OsN_2]^{2+}$  and  $[(NH_3)_5OsN_2Os(NH_3)_5]^{4+}$  form when  $N_2$  is passed through a solution containing  $(NH_3)_5OsOH_2^{3+}$  in the presence of amalgamated zinc as reducing agent.

#### Reference Publications:

1. S. E. Diamond, G. M. Tom, H. Taube, "Ruthenium Promoted Oxidation of Amines." J. Amer. Chem. Soc., 97, 2661 (1975).
2. C. R. Wilson and H. Taube, "Acetate Complexes of Dirhodium and Diruthenium. Aquation and Reduction-Oxidation," Inorg. Chem., 14, 2276 (1975).
3. G. M. Tom and H. Taube, "The Mixed Valence Stated Based on  $\mu$ -Cyanogen-bis(pentaammineruthenium)," J. Amer. Chem. Soc., 97, 5310 (1975).

4. R. H. Magnuson and H. Taube, "Synthesis and Properties of Osmium(II) and Osmium(III) Ammine Complexes of Aromatic Nitrogen Heterocyclics." J. Amer. Chem. Soc., 97, 5129 (1975).
5. R. Kugel and H. Taube, "The Infrared Spectrum and Structure of Matrix-Isolated Sulfur Tetroxide." J. Phys. Chem., 79, 2130 (1975).
6. S. Isied and H. Taube, "The Interaction of HCN with  $(\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O})^{2+}$ ," Inorg. Chem., 14, 2561-2562 (1975).
7. S. Diamond and H. Taube, "Nitrogen to Oxygen Isomerization of the Pentaammineruthenium(III) Glycine Ion." J. Amer. Chem. Soc., 97, 5921 (1975).
8. C. Kuehn and H. Taube, "Ammineruthenium Complexes of Hydrogen Sulfide and Related Sulfur Ligands," J. Amer. Chem. Soc., 98, 689 (1976).
9. H. Taube, "Intramolecular Electron Transfer," Pure and Applied Chemistry, Vol. 44 No. 1 (1975).

66. CRYSTALLOGENICS, SURFACES, STRESS CORROSION CRACKING AND BIOMATERIALS

W. A. Tiller, Professor of Materials Science and Engineering

Professional Associates:

S. Ciraci  
C. F. Jako  
L. Nagel

Graduate Students:

D. G. Boyers	D. N. Modlin
R. Chow	E. M. Young
W. Dibble	

Agency Support:

NSF-Ga-41731  
NSF-DMR74-14650  
NSF/MRL through CMR

Technical Objectives:

(a) To gain a complete and quantitative understanding of the crystallization process by controlling the state of chemical and physical perfection of crystals through control of the freezing process. The ultimate aim is the optimization and control of certain material properties.

(b) To theoretically analyze and experimentally investigate the various contributions which comprise the energy of both a stationary or moving interface between two phases plus how this energy changes with the detailed topography and chemical composition of the interface.

(c) To develop a quantitative predictive theory of corrosion events for gaseous, aqueous and liquid metal environments with the ultimate objective of controlling material properties to avoid cracking.

(d) To develop devices and techniques for monitoring properties of living systems.

Approach:

(a) Theoretical and experimental investigations of all the important elements of the crystallization process: nucleation, interface attachment kinetics, solute transport, fluid motion, interface morphology, physical imperfections and phase equilibria. The experiments are being carried out on a broad range of materials; e.g., stainless steels and other ferrous alloys, garnets, ice, etc., to elucidate the essential physics of the problem.

(b) The excess free energy associated with the interface is treated as a sum of five different parts: (i) a short-range quasi-chemical term due to changes in the orbitals of bound-electron states, (ii) a short-range transition structure term associated with the atomic diffuseness of the interfaces, (iii) a long-range electrostatic term associated with the equalization of the electrochemical potential of the electrons, (iv) a long-range strain term associated with the atomic displacements at the interface and (v) a chemical adsorption term associated with the redistribution of chemical species in the interface field due to (iii). Theoretical and experimental studies are being performed to determine Galvani potential differences between phases, chemical adsorption to surfaces and other factors needed in the evaluation of the accuracy of the theoretical analysis.

(c) A new approach to this important technological subject which utilizes basic understanding of surfaces on an atomistic level and treats the corrosion event (uniform or catastrophic) as a phase transformation. Theoretical models based on this approach allow experimental investigations of the effects of various parameters; e.g., surface energy, stress distribution, composition, grain boundaries and dislocations, etc.

(d) The approach is to develop reliable techniques for monitoring changes in the physiological state of living organisms--humans, animals and plants, via measurements on the external membrane. These changes in physiological state are associated with internal state changes and are registered as electrical, chemical, mechanical or other field variations at the membrane surface.

#### Significant New Research Directions:

(a) Homoepitaxial GaAs films grown by the LPE technique on the (111)B and (100) semi-insulating Cr-doped substrates show a greater net donor concentration for the (111)B orientation than for the (100) orientation. A theoretical explanation of the orientation effect has been found by considering the effect of an interface electric field produced by differential vacancy formation on Ga and As interface sites. This electric field influences both the equilibrium solute partition coefficient and the net interface distribution coefficient when transport across the solid "field-layer" becomes limiting.

(b) The electronic structure of the (111) surface of semiconductors was theoretically investigated using the Bond Orbital Model. The semi-infinite solid was represented by a system which has the two-dimensional periodicity of the (111) surface, but the third dimension was terminated after a finite number of layers, which led to a convergent electronic band structure. Experimental data on Si(111) has been examined in detail. The total densities of states and energy band structures have been determined for ideal, relaxed and (2 x 1) reconstructed Si(111). The lower back-bonding state,  $S_3$ , was found to be localized whether or not the atoms on the surface are relaxed. The effect of the reconstruction was to split the universal surface states,  $S_1$ ,  $S_2$  and  $S_3$  into various bands. In particular, it has been possible to explain various features of the recent angular resolved photoemission from cleaved Si(111) without invoking any new surface states. The surface states of the compound semiconductors; e.g., AlP were found to have similar features to the elemental semiconductors. However, their energy locations depend on the nature of the surface; i.e., anion or cation type.

(c) In the biomaterials area, studies have shown how an inner state change in a human can lead to a set of physiological changes<sup>in the skin</sup> that may be monitored via five unique information channels. Using Kirlian photography as the monitoring tool, we have uncovered the set of equations governing the gas discharge and its modulation via the physiological parameters of the living system under study. Thus, we have

been able to qualitatively explain all the phenomena observed to date by experimenters around the world. It seems as if we are now in a position to write a computer simulation program to point out the size and intensity of the fingerpad halos as one varies the physiological, gas and power supply parameters of the system.

On the experimental side, our previous work was carried out at power supply frequencies of 150 KHz and 1 MHz. At these frequencies, we did not see the anticipated physiological effects that the Soviets claimed. Subsequent theoretical calculations showed us that we should not have expected to see such effects because we were working at too high a frequency range. Thus, we carefully designed and are constructing a new type of power supply that will deliver accurately controlled voltage pulses containing an integral number of either sine, sawtooth or square shaped waves over the frequencies 1 KHz-100 KHz and voltages 0 - 40 Kv with voltage control sensitivity better than 0.01%.

#### Future Research Plans:

Continue all four areas of study with enhanced emphasis in the biomaterials area.

#### Reference Publications:

1. S. Ciraci, I. P. Batra and W. A. Tiller, "Electronic Structure for the (111) Surface of Semiconductors," Phys. Rev. B, 12, 5811 (1975).
2. D. O. Nason and W. A. Tiller, "Orientation Dependence of the Solid/Liquid Interfacial Free Energy in Binary Systems," accepted for publication in Surface Science, 1976.
3. S. Ciraci, I. P. Batra and W. A. Tiller, "Some Effects of Inhomogeneous Strain on Surface Properties of Metals," Surface Science, 1976.
4. S. Ciraci, P. Vasudev and W. A. Tiller, "Bond Orbital Model Calculation for Mixed Semiconducting Compounds," J. of Phys. and Chem. of Solids, 1976.
5. W. A. Tiller, "On the Cross-Pollination of Crystallization Ideas between Metallurgy and Geology," accepted for publication in American Mineralogist, 1976.



6. W. A. Tiller, "Kirlian Photography: Its Scientific Foundations and Future Potentials," to be published in Physiological Physics and Therapies, ed. D. N. Ghista (Marcel Dekker, Inc., New York, 1976).
7. W. A. Tiller, "Present Scientific Understanding of the Kirlian Discharge Process," J. of the Osteopathic Physician, February 1976.
8. W. A. Tiller, "The Positive and Negative Space-Time Frames as Conjugate Systems," in Future Science, eds. S. Krippner and J. White (Doubleday-Anchor, 1976).
9. W. A. Tiller, "New Fields--New Laws," *ibid.*
10. W. A. Tiller, "Kirlian Photography as an Electro-Therapeutics Research Tool," The Intl. J. of Acupuncture and Electro-Therapeutics Research, 1976.
11. W. A. Tiller, "Rationale for an Energy Medicine," J. of Wholistic Healing, 1976.

67. BIOLOGICAL PHYSICS

M. Weissbluth, Associate Professor, Applied Physics

Graduate Students:

C.H.C. Yuen

K.A. Buzard

Agency Support:

NIH 1 RO1AM17577-02

Technical Objective:

To obtain structural information on biological molecules by means of the EXAFS method.

Research Report:

We have investigated the X-ray absorption fine structure (EXAFS) of the following compounds: oxy, deoxy and carbon monoxide hemoglobin solutions, methemoglobin powder, hemin powder, hemin chloride powder, oxidized and reduced cytochrome c solutions at different pH values, oxidized cytochrome c powder, oxidized and reduced hemin solutions at high pH. Signals are detected by absorption and/or fluorescence, the former in a gas-filled ionization chamber and the latter in a solid state detector. The two methods complement one another, since absorption is more suited to samples containing a high concentration of the active element while fluorescence is more appropriate for low concentrations. Data analysis has been carried out by three different methods used singly or in combination: (1) Fourier transform using FFT routines which include weighting (window) functions, (2) curve fitting using least squares methods to establish various parameters e.g. amplitudes, shell radii, phase shifts etc. and (3) maximum entropy techniques to eliminate some of the uncertainties associated with the Fourier transform of a signal of finite range.

By these methods we have been able to compare the heme structures of the various compounds and to note, for example, the difference between oxy and de-oxy hemoglobin, the near identity of oxy and co-hemoglobin, the differences in the cytochrome c structures as a function of pH .

68. FUNDAMENTAL STUDIES OF MAGNETIC MATERIALS

R. L. White, Professor, Electrical Engineering and Materials Science & Engineering

Graduate Students:

C. H. Tsang  
G. O. White

Agency Support:

ONR N0014-75-C-0290

Technical Objective:

To understand the macroscopic properties of magnetic materials in terms of the atomic properties of the constituents, and to design magnetic materials based on this knowledge.

Approach:

Spectroscopic studies, optical and microwave, are made on magnetic atoms or ions. The atomic level information thus obtained is used to explain the macroscopic magnetic properties of magnetic materials composed of these ions. Macroscopic magnetic properties are measured, when necessary, as well as related electrical parameters, such as Hall effect, when relevant. Crystals of interesting composition and properties are grown for exploration.

Fundamental Limitations on Magnetic Domain Wall Velocities

Graduate Students: Geoff O. White  
Ching Tsang

The data rate which can be achieved in bubble domain devices is limited by the rate at which magnetic bubbles can be run past a detection point. This rate is in turn determined by the domain wall velocity achievable, so the fundamental mechanisms limiting domain wall velocities have recently become of considerable interest.

For magnetic materials containing highly damped ions (coupled strongly to the crystalline lattice) domain wall velocities and mobilities can be explained on a viscous damping picture. For low loss materials, like yttrium iron garnet, simple theory predicts domain wall mobilities two orders of magnitude higher than are experimentally observed. In the last three years, this discrepancy has largely been resolved, since theory has been developed which shows that the moving domain wall is subject to complex buckling and curling, leaving energy behind in what might be viewed as magnetic eddies. All these phenomena may be regarded as spin wave instabilities induced in the domain wall by its motion. The spin wave modes of the ferrimagnet extend to very low frequencies and may therefore be degenerate with the precession frequencies typical of domain wall motion, hence readily driven by domain wall motion. The spin wave modes of a canted antiferromagnet occur at higher frequency, and are hence harder to excite. Domain wall motion in canted antiferromagnets (such as  $\text{YFeO}_3$ ) should therefore be possible at much higher velocities than in ferrimagnets (such as the garnets), so we have undertaken to study domain wall velocities and mobilities in canted antiferromagnets. Our study has two branches: (1) the measurement of domain wall velocities in  $\text{YFeO}_3$ , and (2) the characterization of the spin wave spectrum of a canted antiferromagnet by studying antiferromagnetic resonance in  $\text{NaMnF}_3$ . Both studies have proven very fruitful in recent months.

The domain wall velocity measurements have led to some remarkable results. Domain wall velocities versus drive field measurements have been made using a Sixtus and Tonks time-of-transit technique. In such a measurement a domain wall is nucleated at one end of a single crystal bar and its motion detected as it passes a number of coils spaced along the bar. Velocity measurements have been made for Bloch, Néel, and head-to-head domain walls, and over a temperature range from liquid  $\text{N}_2$  temperature to roughly  $400^\circ\text{C}$ . For all three type walls domain wall velocities in excess of  $10^6\text{cm/sec}$  have been observed (compared to maximum velocities on the order of  $10^4\text{cm/sec}$  for garnets) and the domain wall velocity is linear in applied field for velocities up to  $6$  or  $7 \times 10^5\text{cm/sec}$ . The apparent mobility of the head-to-head walls is very high,

approximately 50,000 cm/sec Oe at room temperature, and approximately an order of magnitude higher than the mobility of Bloch or Néel walls. We have established that this higher apparent mobility is spurious, and results from the fact that the stable configuration for a head-to-head wall is not transverse to the bar but at a large angle ( $\sim 80^\circ$ ) to the bar axis. This equilibrium angle is determined by the compromise between lowering demagnetization energy by lowering the change in moment normal to the wall and increasing the exchange energy in the domain wall by increasing domain wall area. The domain wall moving with a velocity  $v$  normal to its plane intercepts the bar wall at a point which moves with  $v' = v/\cos\theta$  where  $\theta$  is the angle of the wall normal to the bar axis, and is  $70^\circ$  to  $80^\circ$  for our samples. The apparent axial velocity is therefore some ten times the actual wall velocity. The domain wall mobilities, Bloch, Néel and Head-to-Head, are then found experimentally to be very similar, and to vary with temperature as  $1/T$  in the temperature domain examined. The  $1/T$  temperature dependence suggests that the relaxation process is a three-boson process, probably two magnons and one phonon. The spin wave spectrum of the canted antiferromagnet containing a domain wall has been calculated, and calculations of the relaxation time based on best known interaction parameters is now in progress.

The antiferromagnetic resonance spectrum of the canted antiferromagnet  $\text{NaMnF}_3$  has been observed at frequencies in the range of 33 to 37 GigaHertz, at temperatures from 4.2°K to above the Néel temperature, 65°K, and in magnetic fields up to 20 K Gauss. This spectrum is of interest to the domain wall kinetics problem because it characterizes the spin wave spectrum to which the domain wall motion delivers energy through relaxation processes.

The canted antiferromagnet has, in zero applied field, two  $k = 0$  antiferromagnetic resonance modes. The lower of these turns downward in frequency for an applied field along the principal spin direction. The upper mode turns upward in frequency for all directions of applied field. We have observed both modes at various temperatures and magnetic fields. From this data, plus static susceptibility and magnetization data, we are able to deduce the interaction parameters characterizing

the magnetic behavior of the canted antiferromagnet, and calculate the spin wave spectrum of the canted antiferromagnet. We are able to obtain the symmetric and antisymmetric exchange parameters, and the orthorhombic magnetic anisotropy parameters. We have also observed and explained some interesting spin flop phenomena. This research is essentially complete, and comprises the Ph.D. thesis of G. O. White. A short publication on this subject has appeared, and a longer one is in preparation.

Reference Publication:

1. Ching H. Tsang, Robert L. White and Robert M. White, "Bloch, Néel and Head-to-Head Domain Wall Mobilities in  $\text{YFeO}_3$ ," 21st Annual Conference on Magnetism and Magnetic Materials, <sup>3</sup>, AIP Conference Proceedings, Number 25 (December 1975).

## SECTION C

### PUBLICATIONS SINCE LAST REPORT

1. H. I. Aaronson, M. G. Hall, D. M. Barnett and K. R. Kinsman, "The Watson-McDougall Shear: Proof that Widmanstätten Ferrite Cannot Grow Martensitically", *Scripta Metallurgica* 9, 705 (1975).
2. \*F. F. Abraham, D. E. Schreiber, M. R. Mruzik and G. M. Pound, "Phase Separation in Fluid Systems by Spinodal Decomposition: A Molecular Dynamics Simulation", *Phys. Rev. Letts.* 36, 261 (1976).
3. P. L. Adams, H. J. Shaw, D. K. Winslow and L. T. Zitelli, "Waveguides for Transverse Resolution in Surface Acoustic Wave Optical Sensors", *Ultrasonics Symposium Proceedings* (1975), p. 153.
4. °O. B. Ajayi, L. E. Nagel, I. D. Raistrick and R. A. Huggins, "Calculation of Motional Activation Energies for Interstitial Ions in the Rutile Structure Using a Minimum Energy Path Model", *J. Phys. Chem. Solids* 37, 167 (1976).
5. A. Amirnazmi and M. Boudart, "Decomposition of Nitric Oxide on Platinum", *J. of Catalysis* 39, 383 (1975).
6. \*R. N. Anderson and N. A. D. Parlee, "Carbothermic Reduction of Refractory Metals", *J. Vac. Sci. and Technol.* 13, 526 (1976).
7. S. R. Aragon and R. Pecora, "Fluorescence Correlation Spectroscopy and Brownian Rotational Diffusion", *Biopolymers* 14, 119 (1975).
8. S. R. Aragon and R. Pecora, "Fluorescence Correlation Spectroscopy as a Probe of Molecular Dynamics", *J. Chem. Phys.* 64, 1791 (1976).
9. S. R. Aragon and R. Pecora, "Theory of Dynamic Light Scattering from Polydisperse Systems", *J. Chem. Phys.* 64, 2395 (1976).
10. O. I. Asubiojo, L. K. Blair and J. I. Brauman, "Tetrahedral Intermediates in Gas Phase Ionic Displacement Reactions at Carbonyl Carbon", *J. Amer. Chem. Soc.* 97, 6685 (1975).
11. J. Attal and C. F. Quate, "Investigation of Some Low Ultrasonic Absorption Liquids", *J. Acoust. Soc. Am.* 59, 69 (1976).

\*Indicates publication was the result of research supported by NSF/MRL program through CMR

°Indicates support by ARPA through CMR.



12. D. M. Barnett and L. B. Freund, "An Estimate of Strike-Slip Fault Friction Stress and Fault Depth from Surface Displacement Data", Bull. Seism. Soc. of Amer. 65 (5), 1259 (1975).
13. D. M. Barnett and J. Lothe, "Line Force Loadings on Anisotropic Half-Spaces and Wedges", Physica Norvegica 8 (1), 13 (1975).
14. C. W. Bates, Jr. and S. Sparks, "Modulation Transfer Function of a 210/70mm Fibre-Optic Output X-ray Image Intensifier Tube", Appl. Opt. Letts. 14, 1484 (1975).
15. °C. W. Bates, Jr., I. Schneider, A. Salau and O. L. Hsu, "Strain-Induced Room Temperature Photoluminescence in CsI and CsI(Na)", Solid State Communications 18, 101 (1976).
16. D. R. Bauer, J. I. Brauman and R. Pecora, "Depolarized Rayleigh Scattering and Orientational Relaxation of Molecules in Solution. IV. Mixtures of Hexafluorobenzene with Benzene and with Mesitylene", J. Chem. Phys. 63, 53 (1975).
17. D. R. Bauer, J. I. Brauman and R. Pecora, "Depolarized Rayleigh Spectroscopy Studies of Relaxation Processes of Polystyrenes in Solution", Macromolecules 8, 443 (1975).
18. D. R. Bauer, B. Hudson and R. Pecora, "Resonance Enhanced Depolarized Rayleigh Scattering from Diphenylpolyenes", J. Chem. Phys. 63, 588 (1975).
19. \*A. Bienenstock, F. Mortyn, S. Narasimhan and S. C. Rowland, "X-ray Diffraction Radial Distribution Studies of Glassy Ge.<sub>42</sub>Se.<sub>58</sub> and Ge.<sub>2</sub>As.<sub>3</sub>Se.<sub>5</sub>", in Frontiers in Materials Science-Distinguished Lectures, Eds. L. E. Murr and C. Stein; Marcel Dekker, publisher, New York (1976), pp. 1-18.
20. N. Bilir, W. A. Phillips and T. H. Geballe, "Thermal Properties of Boron Phases", Proc. of 14th Int. Conf. on Low Temp. Physics, Helsinki, LT-14 (1975).
21. °G. C. Bjorklund, "Effects of Focusing on Third-Order Nonlinear Processes in Isotropic Media", IEEE J. of Quantum Electronics QE-11 (6), 287 (1975)
22. D. M. Bloom, G. W. Bekkers, J. F. Young and S. E. Harris, "Third Harmonic Generation in Phase Matched Alkali Metal Vapors", Appl. Phys. Letts. 26, 687 (1975).
23. D. M. Bloom, J. F. Young and S. E. Harris, "Mixed Metal Vapor Phase Matching for Third Harmonic Generation", Appl. Phys. Letts. 27, 390 (1975).

24. G. H. Blount, M. K. Preis, R. T. Yanada and R. H. Bube, "Photoconductive Properties of Chemically Deposited PbS with Dielectric Overcoatings", J. of Appl. Phys. 46 (8), 3489 (1975).
25. W. L. Bond, C. C. Cutler, R. A. Lemons and C. F. Quate, "Dark Field and Stereo Viewing with the Acoustic Microscope", Appl. Phys. Letts. 27, 270 (1975).
26. M. Boudart, "Concepts in Heterogeneous Catalysis", in Interactions on Metal Surfaces, Ed. O. R. Gomer, New York (1975).
27. M. Boudart, "Heterogeneous Catlysis", Chapter 7 in Physical Chemistry: An Advanced Treatise, Vol. 7, Eds. H. Eyring, W. Jost and D. Henderson, Academic Press (1975).
28. \*M. Boudart, A. Delbouille, J. A. Dumesic, S. Khammouma and H. Topsøe, "Surface, Catalytic and Magnetic Properties of Small Iron Particles. I. Preparation and Characterization of Samples", J. of Catalysis 37, 486 (1975).
29. M. Boudart, E. G. Derouane, V. Indovina and A. B. Walters, "Preparation of Copper on Magnesia Catalysts: An Electron Spin Resonance Study", J. of Catalysis 39, 115 (1975).
30. °M. Boudart and H. S. Hwang, "Solubility of Hydrogen in Small Particles of Palladium", J. of Catalysis 39, 44 (1975).
31. J. I. Brauman, "Acid and Base", McGraw-Hill Yearbook of Science and Technology, McGraw-Hill, New York (1975).
32. W. G. Breiland, M. D. Fayer and C. B. Harris, "Coherence in Multilevel Systems. II. Description of a Multilevel System as Two Levels in Contact with a Population Reservoir", Phys. Rev. A 13, 383 (1976).
33. H. C. Brenner, J. C. Brock, M. D. Fayer and C. B. Harris, "Direct Measurement of the Quantum Yield for the Creation of Mobile Excitons from Localized States Using Optically Detected Electron Spin Coherence", Chem. Phys. Letts. 33, 471 (1975).
34. G. E. Brown and P. M. Fenn, "High Temperature Structural Study of a Homogeneous, Intermediate Composition Alkali Feldspar", Prog. Geol. Soc. Amer. Ann. Mtg. 7, 1012 (1975).
35. °P. Brulet and H. M. McConnell, "Kinetics of Phase Equilibrium in a Binary Mixture of Phospholipids", J. Am. Chem. Soc. 98, 1314 (1976).
36. R. H. Bube, "Electronic Transport in Polycrystalline Films", Ann. Rev. of Mat. Sci. 5, 201 (1975).

37. R. H. Bube, "How Many Data Establish a Model? Electrical Transport in Amorphous  $\text{As}_2\text{Te}_3$  and Polycrystalline PbS", J. Appl. Phys. 47 (5), 2223 (1976).
38. R. H. Bube, "Non-Conventional Heterojunctions for Solar Energy Conversion", in Critical Materials Problems in Energy Production, Ed. C. Stein, Academic Press (1976).
39. R. H. Bube, "Photoconductivity in Amorphous Semiconductors", RCA Review 36, 467 (1975).
40. R. H. Bube, "The Effect of Defects on the Photoconductivity of Solids", J. Electron. Mat. 4, 991 (1975).
41. F. Buch, A. L. Fahrenbruch and R. H. Bube, "Photovoltaic Properties of n-CdSe/p-ZnTe Heterojunctions", Appl. Phys. Letts. 28, 593 (1976).
42. \*M. A. Burke and W. D. Nix, "Plastic Instabilities in Tension Creep", Acta Metallurgica 23, 793 (1975).
43. R. L. Byer, "Initial Experiments with a Laser Driven Stirling Engine", 2nd NASA Conf. on Laser Energy Conversion, NASA/Ames Research Center, Moffett Field, California (1975).
44. R. L. Byer, "Remote Air Pollution Measurement", Proceedings ICO Conf. on Opt. Methods in Sci. and Indust. Measure., Tokyo (1974); also Japan J. Appl. Phys. 14 (1975) and Optical and Quantum Electronics 7, 147 (1975).
45. R. D. Caligiuri, R. T. Whalen and O. D. Sherby, "Superplastic Hot Pressing of White Cast Iron", The Int. J. of Powder Metallurgy and Powder Technology 12, 9 (1976).
46. C. A. Carter, P. Frank, T. K. Eccles, M. M. Yevitz and K. O. Hodgson, "Structural and Electrochemical Studies on (Glycylglycyl Histidine) Cu(II)", Inorg. Chem. 15 (1976).
47. \*D. R. Carter and W. C. Hayes, "Fatigue Life of Compact Bone - I. Effects of Stress Amplitude, Temperature and Density", J. Biomechanics 9, 27 (1976).
48. \*D. R. Carter, W. C. Hayes and D. J. Schurman, "Fatigue Life of Compact Bone - II. Effects of Microstructure and Density", J. Biomechanics 9, 211 (1976).
49. H. C. Casey, Jr. and G. L. Pearson, "Diffusion in Semiconductors", in Defects in Solids, Vol. II, Eds. J. H. Crawford and L. M. Slifkin, Plenum Press, New York (1975), pp. 163-255.

50. I. Chabay, G. Klauminzer and B. S. Hudson, "Coherent Anti-Stokes Raman Spectroscopy (CARS): Improved Experimental Design and Observation of New Higher Order Processes", Appl. Phys. Letts. 28, 27 (1976).
51. D. J. Chadi, R. M. White and W. A. Harrison, "Theory of the Magnetic Susceptibility of Tetrahedral Semiconductors", Phys. Rev. Letts. 35, 17 (1975).
52. C. W. Chu, T. H. Geballe, S. Early, R. E. Schwall and A. Rusakov, "High Pressure Metallic Phase in Cuprous Chloride Single Crystals", J. Phys. Chem. 8, L241 (1975).
53. P. W. Chye, I. A. Babalola, T. Sukegawa and W. E. Spicer, "GaSb Surfaces States and Schottky-Barrier Pinning", Comments-Phys. Rev. Letts. 35, 1600 (1975).
54. S. Ciraci, I. P. Batra and W. A. Tiller, "Electronic Structure for the (111) Surface of Semiconductors", Phys. Rev. B 12, 5811 (1975).
55. S. Ciraci, I. P. Batra and W. A. Tiller, "Some Effects of Inhomogeneous Strain on Surface Properties of Metals", Surface Science (1976).
56. S. Ciraci, P. Vasudev and W. A. Tiller, "Bond Orbital Model Calculation for Mixed Semiconducting Compounds", J. of Phys. and Chem. of Solids (1976).
57. °U. Cohen and R. A. Huggins, "Silicon Epitaxial Growth by Electrodeposition from Molten Fluorides", J. Electrochem. Soc. 123, 381 (1976).
58. L. A. Coldren and H. J. Shaw, "Surface Wave Long Delay Lines", Proc. IEEE 64 (5), 598 (1976).
59. D. M. Collins, J. B. Lee and W. E. Spicer, "Study of the Hydrogenation of O Adsorbed on Pt", J. Vac. Sci. Technol. 13, 266 (1976).
60. \*D. M. Collins, J. B. Lee and W. E. Spicer, "Use of Photoemission, Auger, and Thermal-Desorption Techniques to Study the Mechanism of a Catalytic Reaction", Phys. Rev. Letts. 35, 592 (1975).
61. °J. P. Collman, "Disodium Tetracarbonylferrate--A Transition Metal Analogue of Grignard's Reagent", Accounts Chem. Res. 8, 342 (1975).
62. J. P. Collman, J. I. Brauman and K. S. Suslick, "Oxygen Binding to Iron Porphyrins", J. Amer. Chem. Soc. 97, 7185 (1975).
63. J. P. Collman, P. A. Christian, S. Current, P. Denisevich, T. R. Halbert, E. R. Schmittou and H. O. Hodgson, "The Molecular Structure of trans-Methyliodo[difluoro[3,3'-trimethylene dinitrilo)-di-2-pentanone dioximate]borate} rhodium(III)", Inorg. Chem. 15, 223 (1976).

64. J. P. Collman, R. R. Gagne, C. A. Reed, K. Spartalian and G. Lang, "Mössbauer Spectroscopy of Hemoglobin Model Compounds: Evidence for Conformational Excitation", J. Chem. Phys. 12, 5375 (1975).
65. J. P. Collman, J. L. Hoard, N. Lim, G. Lang and C. A. Reed, "The Synthesis, Stereochemistry, and Structure-Related Properties of  $\alpha, \beta, \gamma, \delta$ -Tetraphenylporphyrinatoiron(II)", J. Amer. Chem. Soc. 97, 2676 (1975).
66. J. P. Collman and T. N. Sorrell, "A Model for the Carbonyl Adduct of Ferrous Cytochrome P-450", J. Amer. Chem. Soc. 97, 4133 (1975).
67. J. P. Collman, T. N. Sorrell, J. H. Dawson, J. R. Trudell, E. Bunnenberg and C. Djerassi, "Magnetic Circular Dichroism of the Ferrous Carbonyl Adducts of Cytochrome P-450 and P-420 and Their Synthetic Models; Further Evidence for Mercaptide as the Fifth Ligand to Iron", Proc. Nat. Acad. Sci. US 73, 6 (1976).
68. J. C. Conrad and P. J. Flory, "Moments and Distribution Functions for Polypeptide Chains. Poly-L-alanine", Macromolecules 9, 41 (1976).
69. \*B. A. Coyle, J. A. Koperski and R. N. Anderson, "A Technical and Economic Analysis of Processes for the Recovery of Metal in the Non-Ferrous Portion of Automobile Shredder Refuse", Proc. of the Fifth Annual Mineral Waste Utilization Symposium (1976).
70. S. Cramer, D. Burland and B. S. Hudson, "A Polarized Single Crystal Raman Study of the Librational Phonons in p-Diodobenzene", J. Chem. Phys. 64, 1140 (1976).
71. S. P. Cramer, T. K. Eccles, F. Kutzler, K. O. Hodgson and S. Doniach, "Applications of X-ray Photoabsorption Spectroscopy to the Determination of Local Structure in Organometallic Compounds", J. Amer. Chem. Soc. 98 (1976).
72. S. P. Cramer, T. K. Eccles, F. Kutzler, K. O. Hodgson and M. Kline, "Electronic and Structural Studies of Metal Ions in Biological Macromolecules Using X-ray Absorption Spectroscopy", Advances in Chemistry Series, Am. Chem. Soc. (1976).
73. S. P. Cramer, T. K. Eccles, F. Kutzler, K. O. Hodgson, and L. E. Mortenson, "Mo X-ray Absorption Edge Spectra - The Chemical State of Mo in Nitrogenase", J. Amer. Chem. Soc. 98, 1287 (1976).
74. R. A. Dalla Betta and M. Boudart, "Infrared Examination of the Reversible Oxidation of Ferrous Ions in Y Zeolite", J. Catal. 41, 40 (1976).
75. B. H. W. S. deJong and G. E. Brown, "Molecular Orbital Studies of  $(\text{Si}, \text{Al})_{207}$  Groups in Silicates", EOS, Trans. Amer. Geophys. Union 56, 1076 (1976).

76. C. S. DeSilets, J. Fraser and G. S. Kino, "Transducer Arrays Suitable for Acoustic Imaging", IEEE Ultrasonics Symp. Proc. (1975).
77. S. Diamond and H. Taube, "Nitrogen to Oxygen Isomerization of the Pentaamineruthenium(III) Glycine Ion", J. Amer. Chem. Soc. 97, 5921 (1975).
78. S. E. Diamond, G. M. Tom and H. Taube, "Ruthenium Promoted Oxidation of Amines", J. Amer. Chem. Soc. 97, 2661 (1975).
79. R. J. DiMelfi and W. D. Nix, "Hole Growth in Plane Viscous Creep Including Interaction Effects", Int. J. Solids Structures 12, 217 (1976).
80. \*D. D. Dlott and M. D. Fayer, "Experimental Determination of the Triplet Exciton Intermolecular Interaction Matrix Element and the Exciton-Phonon Scattering Rate in Molecular Crystals", Chem. Phys. Letts. (1976).
81. R. T. Dodd, J. E. Grover and G. E. Brown, "Pyroxenes in the Shaw (L-7) Chondrite", Geochim. Cosmochim. Acta 39, 1585 (1975).
82. S. Doniach, I. Lindau, W. E. Spicer and H. Winick, "Synchrotron Radiation as a New Tool Within Photon-Beam Technology", J. Vac. Sci. Technol. 12, 1123 (1975).
83. °J. A. Dumesic and M. Boudart, "Catalytic Synthesis and Decomposition of Ammonia", in The Catalytic Chemistry of Nitrogen Oxides, Eds. R. L. Klimisch and J. G. Larson, Plenum Publishing Corp., New York (1975), pp. 95-106.
84. \*J. A. Dumesic, H. Topsøe, and M. Boudart, "Surface, Catalytic and Magnetic Properties of Small Iron Particles. III. Nitrogen Induced Surface Reconstruction", J. of Catalysis 37, 513 (1975).
85. \*J. A. Dumesic, H. Topsøe, S. Khammouma and M. Boudart, "Surface, Catalytic and Magnetic Properties of Small Iron Particles. II. Structure Sensitivity of Ammonia Synthesis", J. of Catalysis 37, 503 (1975).
86. L. B. Ebert, R. A. Huggins and J. I. Brauman, "Reaction of Antimony Pentafluoride with Poly (Carbon Monofluoride)", Mat. Res. Bull. 11, 615 (1976).
87. G. R. Edwards, T. R. McNelley and O. D. Sherby, "Diffusion Controlled Deformation of Particulate Composites", Philosophical Mag. 32, 1245 (1975).
88. L. Elias, W. M. Fairbank, J. M. Madey, H. A. Schwettman and T. Smith, "Observation of Stimulated Emission of Radiation by Relativistic Electrons in a Spatially Periodic Transverse Magnetic Field", Phys. Rev. Letts. 36, 717 (1976).

89. A. G. Elliot and R. A. Huggins, "Phases in the System  $\text{NaAlO}_2\text{-Al}_2\text{O}_3$ ", J. Amer. Ceramic Soc. 58 (11), 497 (1975).
- 90.\*°D. Elwell, R. C. DeMattei, I. V. Zubeck, R. S. Feigelson and R. A. Huggins, "DC Resistances in Electrolytic Crystallization from Molten Salts", J. Crystal Growth 33, 232 (1976).
- 91.\*°D. Elwell, I. V. Zubeck, R. S. Feigelson and R. A. Huggins, "Surface Structure and Electrolytic Growth Stability of  $\text{LaB}_6$  Crystals", J. Crystal Growth 29, 65 (1975).
92. A. L. Fahrenbruch, F. Buch, K. Mitchell and R. H. Bube, "II-VI Photovoltaic Heterojunctions for Solar Energy Conversion", 11th IEEE Photovoltaic Specialists Conference, p. 450 (1975).
93. S. A. Farnow and B. A. Auld, "An Acoustic Phase Plate Imaging Device", Acoustical Holography 6, 259 (1975).
94. \*M. D. Fayer and C. R. Gochanour, "On the Temperature Dependence of Excited Triplet State Spin Sublevel Populations of Shallow Traps in Molecular Crystals", J. Chem. Phys. (1976).
95. \*R. S. Feigelson, "The Growth of Ternary Semiconductor Crystals Suitable for Device Applications", J. Physique Colloq. 36, C3 (1975).
96. P. M. Fenn, "The Effect of Pressure on the Monoclinic Alkali Feldspar Lattice", EOS, Trans. Amer. Geophys. Union 56, 1077 (1976).
97. P. M. Fenn and G. E. Brown, "Energetics of the Alkali Site in K-Na Feldspars", Prog. Geol. Soc. Amer. Ann. Mtg. 7, 1071 (1975).
98. P. J. Flory, "Introductory Lecture", Faraday Discussions of the Chemical Society 57, 7 (1974).
99. P. J. Flory, "Spatial Configuration of Macromolecular Chains", Science 188, 1268 (1975).
100. P. J. Flory and V. W. C. Chang, "Moments and Distribution Functions for Poly(dimethylsiloxane) Chains of Finite Length", Macromolecules 9, 33 (1976).
101. C. M. Fortunko and H. J. Shaw, "One Millisecond Surface Acoustic Wave Delay Line", Ultrasonics Symp. Proc., p. 573 (1975).
102. J. Fraser, J. Havlice, G. Kino, W. Leung, H. Shaw, K. Toda, T. Waugh, D. Winslow and L. Zitelli, "An Electronically Focused Two-Dimensional Acoustic Imaging System", Acoustical Holography 6, 275 (1975).
102. °J. G. Fripiat, K. T. Chow, M. Boudart, J. B. Diamond and K. H. Johnson, "The Structure and Bonding of Lithium Clusters", J. of Molecular Catalysis 1, 59 (1975/76).

103. A. Fuwa, R. N. Anderson and N. A. D. Parlee, "Thermodynamics of Nitride Formation in Liquid U-Gd-Sn Alloys", J. of High Temp. Sci. 7, 249 (1975).
104. \*S. D. Gavazza and D. M. Barnett, "The Image Force on a Dislocation Loop in a Bounded Elastic Medium", Scripta Met. 9, 1263 (1975).
105. P. E. Gregory, P. Chye, H. Sunami and W. E. Spicer, "The Oxidation of Cs UV Photoemission Studies", J. Appl. Phys. 46, 3525 (1975).
106. P. E. Gregory and W. E. Spicer, "Photoemission Studies of the GaAs-Cs Interface", Phys. Rev. B 12, 2370 (1975).
107. P. E. Gregory and W. E. Spicer, "Photoemission Study of Surface States of the (110) GaAs Surface", Phys. Rev. B 13, 725 (1976).
108. P. E. Gregory and W. E. Spicer, "Photoemission Study of the Adsorption of O<sub>2</sub>, CO and H<sub>2</sub> on GaAs (110)", Surface Sci. 54, 229 (1976).
109. P. E. Gregory and W. E. Spicer, "Ultraviolet Photoemission Study of Cesium Oxide Films on GaAs", J. Appl. Phys. 47, 510 (1976).
110. D. HaferBurns, A. Bienenstock and S. C. Rowland, "Radial Distribution Studies of Ge-Sn-S and Ge-Pb-S Glasses", Bull. Amer. Phys. Soc. 21, 467 (1976).
111. T. Halicioglu and G. M. Pound, "Calculation of Potential Energy Parameters from Crystalline State Properties", Phys. Stat. Sol. a 30, 619 (1975).
112. \*A. Hallak, R. H. Hammond, R. B. Zubeck and T. H. Geballe, "Superconductivity and Range of Existence of the Al<sub>5</sub> Phase in the Nb-Ge System", Bull. Amer. Phys. Soc. 21, 340 (1976).
113. J. M. E. Harper, T. H. Geballe and F. J. DiSalvo, "Heat Capacity of 2H-NbSe<sub>2</sub> at the Charge Density Wave Transition", Phys. Letts. 54A, 27 (1975).
114. W. A. Harrison, "Review of Metal-Insulator Transitions (N. F. Mott) and Electrical Conduction in Solid Materials (J. P. Suchet)", Physics Today 29, 53 (1976).
115. W. A. Harrison, "Surface Reconstruction Semiconductors", Surface Science 55, 1 (1976).
116. \*W. C. Hayes and D. R. Carter, "The Effect of Marrow on Energy Absorption of Trabecular Bone", Trans. Orthopaedic Research Society 1, 10 (1976).
117. W. C. Hayes, L. W. Swenson and D. J. Schurman, "Mechanics of Tibial Plateau Fractures", Trans. Orthopaedic Research Society 1, 11 (1976).



118. C. R. Helms and R. J. Madix, "Molecular Beam Relaxation Spectrometry (MBRS) Measurement of the Desorption Rate Constant for CO on Ni(110)", *Surface Science* 52, 677 (1975).
119. C. R. Helms, K. Y. Yu and W. E. Spicer, "Further Evidence for Equilibrium Surface Segregation in the Cu-Ni Alloys-CO and H<sub>2</sub> Chemisorption", *Surface Sci.* 52, 217 (1975).
120. M. A. Henesian, R. L. Herbst and R. L. Byer, "Optically Pumped Superfluorescent Na<sub>2</sub> Molecular Laser", *J. Appl. Phys.* 47 (4), 1515 (1976).
121. K. O. Hodgson and J. D. Dunitz, "Structural Studies of Synthetic Corrinoids, IV. Molecular Structure of a Novel Oxo-bridged Nickel (II) Corrinoid Complex", *Helv. Chim. Acta* 59, 000 (1976).
122. K. O. Hodgson, J. C. Phillips and A. Wlodawer, "Applications of Synchrotron Radiation to X-ray Diffraction Studies of Proteins", *Trans. Amer. Crystallographic Assoc., Proc. of the Symp. on Instruments for Tomorrow's Crystallography* 12 (1976).
123. E. Honea and A. M. Johnson, "A Theory of Concentric, Kink, and Sinusoidal Folding and of Monoclinical Flexuring of Compressible, Elastic Multilayers. Part IV. Development of Sinusoidal and Kink Folds in Multilayers Confined by Rigid Boundaries", *Tectonophysics* (1976).
124. O. L. Hsu and C. W. Bates, Jr., "Luminescence Phenomena in CsI(Na)", *J. of Luminescence* 11, 65 (1975).
125. K. S. Hsu, A. H. Kung, L. J. Zych, J. F. Young and S. E. Harris, "1202.8Å Generation in Hg Using a Parametrically Amplified Dye Laser", *IEEE J. Quant. Elect.* QE-12, 60 (1976).
126. B. Hudson, J. Diamond and J. N. A. Ridyard, "Polyene Spectroscopy: Photoelectron Spectra of the Diphenylpolyenes", *J. Am. Chem. Soc.* 98, 1126 (1976).
127. B. Hudson and R. Jacobs, "The Ultraviolet Transitions of the Ehtidium Cation", *Biopolymers* 14, 1309 (1975).
128. B. Hudson, H. Karp and S.-H. Chen, "Pseudorotational Motion of Methylcyclopentane Observed by Neutron Inelastic Scattering", *J. Chem. Phys.* 62, 4564 (1975).
129. R. A. Huggins, "Alkali Ion Transport in Materials of the Beta Alumina Family", in *Mass Transport Phenomena in Ceramics*, Eds. A. R. Cooper and A. H. Heuer, Plenum Press (1975), p. 155.
130. R. A. Huggins, "Basic Research in Materials", *Science* 191, 647 (1976).

131. G. M. K. Humphries and H. M. McConnell, "Antibodies Against Nitroxide Spin Labels", *Biophysical Journal* 16, 275 (1976).
132. G. M. K. Humphries and H. M. McConnell, "Antigen Mobility in Membranes and Complement-Mediated Immune Attack", *Proc. Nat. Acad. Sci. USA* 72, 2483 (1975).
133. S. H. Hunter and A. I. Bienenstock, "EXAFS Studies of Amorphous Semiconductors", *Bull. Amer. Phys. Soc.* 21, 676 (1976).
134. I. C. Huseby, S. E. Hsu, T. R. McNeley, G. R. Edwards, D. Francois, J. C. Shyne and O. D. Sherby, "Yield Points and Strain Aging in Hexagonal-Based Particulate Composites", *Met. Trans.* 6A, 2005 (1975).
135. M. Ilegems and G. L. Pearson, "Phase Studies in III-IV, II-VI and IV-VI Compound Semiconduction Alloy Systems", *Ann. Rev. of Materials Science* 5, 345 (1975).
136. S. Isied and H. Taube, "The Interaction of HCN with  $(\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O})^{2+}$ ", *Inorg. Chem.* 14, 2561 (1975).
137. T. Jach, "Detection of Nuclear Quadrupole Resonances via Induced Longitudinal Magnetization", *Appl. Phys. Letts.* 28, 49 (1976).
138. R. E. Jacobs, B. Hudson and H. C. Andersen, "A Theory of the Chain Melting Phase Transition of Aqueous Phospholipid Dispersions", *Proc. Nat. Acad. Sci. USA* 72, 3993 (1975).
139. J. S. Johannessen, W. E. Spicer and Y. E. Strausser, "A Study of the Chemical Composition of MOS and MNOS Structures by Auger Electron Spectroscopy", *Thin Solid Films* 32, 311 (1976).
140. J. S. Johannessen, W. E. Spicer and Y. E. Strausser, "Phase Separation in Silicon Oxides as Seen by Auger Electron Spectroscopy", *Appl. Phys. Letts.* 27, 452 (1975).
141. A. M. Johnson and B. M. Page, "A Theory of Concentric, Kink, and Sinusoidal Folding and of Monoclinal Flexuring of Compressible, Elastic Multilayers. Part VII. Development of Folds in Huasna Syncline, Santa Maria, California", *Tectonophysics* (1976).
142. B. T. Khuri-Yakub, G. S. Kino and P. Galle, "Studies of the Optimum Conditions for Growth of RF Sputter ZnO Films", *J. Appl. Phys.* 46, 3266 (1975).
143. G. S. Kino, "A Review of Some Possible Applications of Acoustic Convolver Technology", *Proc. Reunion Internationale Organisee par la DRME*, p. 113 (1976).
144. G. S. Kino, "Acoustoelectric Interactions in Acoustic Surface Wave Devices", *Proc. IEEE, Special Issue on Acoustic Wave Technology* (1976).

145. G. S. Kino, "Applications of Electronically Scanned Acoustic Imaging Techniques to NDE", Proc. ARPA/AFML Review of Quantitative NDE, p. 303 (1976).
146. G. S. Kino, C. DeSilets, J. Fraser and T. Waugh, "New Acoustic Imaging Systems for Non-destructive Testing", IEEE Ultrasonics Symp. Proc. (1975).
147. R. A. Klemm and M. R. Beasley, "Theory of the Upper Critical Field in Layered Superconductors", Phys. Rev. B 12, 877 (1975).
148. °W. Kleeman and H. M. McConnell, "Interactions of Proteins and Cholesterol with Lipids in Bilayer Membranes", Biochim. et Biophys. Acta 491, 206 (1976).
149. \*R. Koch, "A Replication Technique for Studies of Bone in Reflected Light", Practical Metallography 13, 72 (1976).
150. H. Komine and R. L. Byer, "Proposed Atomic Mercury Anti-Stokes Frequency Converter", Appl. Phys. Letts. 27, 5 (1975).
151. B. Krautler, A. Pfaltz, R. Nordmann, K. O. Hodgson, J. D. Dunitz and A. Eschenmosher, "Versuche zur Redox-Simulation der Photochemischen A/D Secocorrin-Corrin-Cycloisomerisierung", Helv. Chim. Acta 59, 924 (1976).
152. \*M. N. Kronick and W. A. Little, "A New Immunoassay Based on Fluorescence Excitation by Internal Reflection Spectroscopy", J. Immunological Methods 8, 235 (1975).
153. C. Kuehn and H. Taube, "Ammineruthenium Complexes of Hydrogen Sulfide and Related Sulfur Ligands", J. Amer. Chem. Soc. 98, 689 (1976).
154. R. Kugel and H. Taube, "The Infrared Spectrum and Structure of Matrix-Isolated Sulfur Tetroxide", J. Phys. Chem. 79, 2130 (1975).
155. °P. G. Kury and H. M. McConnell, "Regulation of Membrane Flexibility in Human Erythrocytes", Biochemistry 14 (13), 2798 (1975).
156. E. H. Lee, "Thermo-viscoelasticity", in Mechanics of Visco-elastic Media and Bodies, Ed. J. Hult, Springer-Verlag (1975), p. 339.
157. E. H. Lee, "Wave Propagation in Composites with Periodic Structures", Proc. CANCAM 75, Ed. G. Dhatt (1975), p. G49.
158. E. H. Lee, B. Budiansky and D. C. Drucker, "On the Influence of Material Properties on Stress Wave Propagation through Elastic Slabs", J. Appl. Mech. 42, 417 (1975).

159. E. H. Lee, H. Poppa and G. M. Pound, "Quantitative Measurements of Nucleation and Growth Kinetics of Gold on Mica", *Thin Solid Films* 32, 229 (1976).
160. R. A. Lemons and C. F. Quate, "Acoustic Microscopy - A Tool for Medical and Biological Research", in *Acoustical Holography*, Vol. 6, Ed. N. Booth, Plenum Press, New York (1975). p. 305.
161. W. P. Leung, R. A. Mills, H. J. Shaw, D. K. Winslow and L. T. Zitelli, "Non-destructive Testing with an Electronically Focused Acoustic Imaging System", *Ultrasonics Symp. Proc.*, p. 84 (1975).
162. D. B. Lidow, R. W. Falcone, J. F. Young and S. E. Harris, "Inelastic Collision Induced by Intense Optical Radiation", *Phys. Rev. Letts.* 36, 462 (1976).
163. B. E. Liebert and R. A. Huggins, "Ionic Conductivity of  $\text{Li}_4\text{GeO}_4$ ,  $\text{Li}_2\text{GeO}_3$  and  $\text{Li}_2\text{Ge}_7\text{O}_{15}$ ", *Mat. Res. Bull.* 11, 533 (1976).
164. W. Y. Lim, J. D. Khazzoom and R. N. Anderson, "Evaluation of Mineral Waste Utilization Processes and Strategies by Net Energy", *Proc. of the Fifth Annual Mineral Waste Utilization Symposium* (1976).
- 165.\*A. L. Lin and R. H. Bube, "Effects of Heat Treatment and Plastic Deformation on the Photoelectronic Properties of High-Resistivity GaAs:Cr", *J. of Appl. Phys.* 46 (12), 5302 (1975).
- 166.\*A. L. Lin and R. H. Bube, "Photoelectronic Properties of High-Resistivity GaAs:Cr", *J. Appl. Phys.* 47 (5), 1859 (1976).
- 167.\*A. L. Lin, E. Omelianovski and R. H. Bube, "Photoelectronic Properties of High-Resistivity GaAs:O", *J. Appl. Phys.* 47 (5), 1852 (1976).
- 168.\*S. F. Lin, W. E. Spicer and G. H. Schechtman, "Electron Escape Depth, Surface Composition and Charge Transfer in Tetrathiafulvalene Tetracyanoquinodimethane (TTF-TCNQ) and Related Compounds: Photoemission Studies", *Phys. Rev. B* 12, 4184 (1975).
- 169.\*I. Lindau, P. Pianetta, K. Y. Yu and W. E. Spicer, "Photoemission of Gold in the Energy Range 30-300 eV Using Synchrotron Radiation", *Phys. Rev. B* 13, 492 (1976).
- 170.\*I. Lindau, P. Pianetta, K. Y. Yu and W. E. Spicer, "Photoemission from Some Metals and Semiconductors in the Energy Range 5-350 eV", *J. Vac. Sci. Technol.* 13, 269 (1976).
- 171.\*I. Lindau, P. Pianetta, K. Yu and W. E. Spicer, "The Intrinsic Linewidth of the 4f Levels in Gold as Determined by Photoemission", *Phys. Letts.* 54A, 47 (1975).

172. W. A. Little and R. Lorentz, "Solid Bis(1,10-phenanthroline) platinum(II)-and Bis(2,2'-bipyridyl)platinum(II)Platinates(II) with Intermolecular Metal-Metal Interactions", *Inorganica Chimica Acta* 18, 3 (1976).
173. W. A. Little and G. L. Shaw, "A Statistical Theory of Short and Long Term Memory", *Behavioral Biology* 14, 115 (1975).
174. \*J. Lothe and D. M. Barnett, "On the Existence of Surface Wave Solutions for Anisotropic Elastic Half-Spaces", *J. Appl. Phys.* 47, 428 (1976).
175. R. W. Lund and W. D. Nix, "On High Creep Activation Energies for Dispersion Strengthened Metals", *Met. Trans.* 6A, 1329 (1975).
176. R. J. Madix, "Catalytic Reactions on Metal Surfaces, A Review of the Recent Contributions of Surface Science", *J. Vac. Sci. Technol.* 13 (1) (1976).
177. \*R. J. Madix, J. L. Falconer and A. M. Suszko, "The Autocatalytic Decomposition of Acetic Acid on Ni(110)", *Surface Science* 54, 6 (1976).
178. \*R. J. Madix and J. L. Falconer, "Surface Stabilized Reaction Intermediate: Formic Anhydride", *Surface Science* 51, 546 (1975).
179. R. H. Magnuson and H. Taube, "Synthesis and Properties of Osmium(II) and Osmium(III) Ammine Complexes of Aromatic Nitrogen Heterocyclics", *J. Amer. Chem. Soc.* 97, 5129 (1975).
180. D. M. Mason and P. E. Depoy, "Periodicity in Chemically Reacting Systems: A Model for the Kinetics of the Decomposition of  $\text{Na}_2\text{S}_2\text{O}_4$ ", *Faraday Symposia of the Chemical Society* 9, 47 (1975).
181. D. M. Mason and B. G. Ong, "Numerical Solution of Equations Arising in Energy Transport in Nonequilibrium Chemically Reacting Systems", *Chem. Eng. Sci.* (1976).
182. D. M. Mason, S. Pancharatnam and R. A. Huggins, "Catalytic Decomposition of Nitric Oxide on Zirconia by Electrolytic Removal of Oxygen", *J. Electrochem. Soc.* 122, 869 (1975).
183. D. K. Matlock and W. D. Nix, "Effects of Helium on the High-Temperature Creep and Fracture Properties of Ni-6%W", *J. of Nuclear Materials* 56, 145 (1975).
184. B. L. Mattes, "Atom Clustering and Stacking Formations on Interfaces", *J. Vac. Sci. Technol.* 13 (1976).
185. B. L. Mattes, "Liquid-Solid Interfaces During Epitaxial Nucleation and Growth of III-V Compounds", *Crit. Rev. Solid State Sci.* 5, 457 (1975).

186. B. L. Mattes, Y. M. Hounq and G. L. Pearson, "Growth and Properties of Semi-Insulating Epitaxial GaAs", J. Vac. Sci. Technol. 12, 869 (1975).
187. G. M. Mavko and A. Nur, "Melt Squirt in the Asthenosphere", J. Geophys. Res. 88, 1444 (1975).
188. \*J. G. McCarty and R. J. Madix, "Formic Acid Desorption from Graphitized Ni(110)", Surface Science 54, 210 (1976).
189. \*J. G. McCarty and R. J. Madix, "The Adsorption of CO, H<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O on Carburized and Graphitized Ni(110)", Surface Science 54, 121 (1976).
190. °H. M. McConnell, "Role of Lipid in Membrane Structure and Function", in Cellular Membranes and Tumor Cell Behavior, Proc. 28th Annual Symposium in Fundamental Cancer Research, University of Texas M.D. Anderson Hospital and Tumor Institute, Houston (1975), pp. 61-80.
191. \*W. H. McConnell, "Sufficient Conditions for the Identification of Dislocation Burgers Vectors Using Computer Electron Micrographs", Philosophical Mag. 33, 863 (1976).
192. A. Miller, "An Inelastic Constitutive Model for Monotonic, Cyclic, and Creep Deformation: Part I - Equations Development and Analytical Procedures", J. of Eng. Mat. and Tech. 98, 97 (1976).
193. A. Miller, "An Inelastic Constitutive Model for Monotonic, Cyclic, and Creep Deformation: Part II - Application of Type 304 Stainless Steel", J. of Eng. Mat. and Tech. 98, 106 (1976).
194. A. K. Miller and O. D. Sherby, "On Subgrain Strengthening at High and Low Temperatures", Scripta Met. 10, 311 (1976).
195. \*J. Miyazaki, J. A. Barker and G. M. Pound, "Monte Carlo Calculation of the Surface Tension and Chemical Potential of Lennard-Jones Argon", J. Chem. Phys. 64, 3334 (1976).
196. \*D. F. Moore, M. R. Beasley and J. M. Rowell, "Tunneling Studies of Nb<sub>3</sub>Sn Films in Parallel Magnetic Fields", Bull. Am. Phys. Soc. 21, 403 (1976).
197. \*M. R. Mruzik, F. F. Abraham, D. E. Schreiber and G. M. Pound, "A Monte Carlo Study of Ion-Water Clusters", J. of Chem. Phys. 64, 481 (1976).
198. W. D. Nix, "On the Possible Relation Between Grain Boundary Migration and the Kinetics of Grain Boundary Sliding in Polycrystals", Rate Processes in Plastic Deformation of Materials, ASM (1975).
199. A. Nur, "A Note on the Constitutive Law for Dilatancy", Pageophy. 113, 197 (1975).

200. S. T. Pantelides and W. A. Harrison, "Electronic Structure, Spectra and Properties of 4:2-coordinated Materials. I. Crystalline and Amorphous  $\text{SiO}_2$  and  $\text{GeO}_2$ ", Phys. Rev. B 13, 15 (1976).
201. \*C. J. Park, J. E. Mahan, R. T.-S. Shiah, H. A. VanderPlas and R. H. Bube, "Electronic Transport in Amorphous Germanium Arsenides", J. Appl. Phys. 46 (12), 5307 (1975).
202. G. A. Parks, "Adsorption in the Marine Environment", Chapter 4 in Marine Geochemistry, Vol. 1, Eds. J. P. Riley and G. Skirrow, Academic Press (1975).
203. J. C. Phillips, A. Wlodawer, M. Yevitz and K. O. Hodgson, "Applications of Synchrotron Radiation to Protein Crystallography: Preliminary Results", Proc. Nat. Acad. Sci. USA 73, 128 (1976).
204. P. Pianetta, I. Lindau, C. Garner and W. E. Spicer, "Determination of the Oxygen Binding Site on GaAs (110) Using Soft X-ray Photoemission Spectroscopy", Phys. Rev. Letts. 35, 1356 (1975).
205. M. A. Piestrup, R. A. Powell, G. B. Rothbart, C. K. Chen and R. H. Pantell, "Cerenkov Radiation as a Light Source for the 2000 to 620Å Spectral Range", Appl. Phys. Letts. 28 (1976).
206. J. D. Plummer and J. D. Meindl, "A Monolithic 200 Volt CMOS Analog Switch", Int. Solid State Circuits Conf., Conference Digest (1976), Pp. 214-215.
207. G. G. Poe and A. Acrivos, "Closed Streamline Flows Past Rotating Single Cylinders and Spheres: Inertia Effect", J. Fluid Mech. 72, 605 (1975).
208. G. G. Poe and A. Acrivos, "Closed Streamline Flows Past Small Rotating Particles: Heat Transfer at High Peclet Numbers", Int. J. Multiphase Flow 2, 365 (1976).
209. D. E. Post, W. Hetherington and B. Hudson, "100 eV Electron Impact Spectra of Hexatriene", Chem. Phys. Letts. 35, 259 (1975).
210. R. A. Powell and W. E. Spicer, "Photoemission Investigation of Surface States on Strontium Titanate", Phys. Rev. B 13, 2601 (1976).
211. P. Protopapas, H. C. Andersen and N. A. D. Parlee, "Theory of Transport in Liquid Metals. II. Calculation of Shear Viscosity Coefficients", Chem. Phys. 8, 17 (1975).
212. P. Protopapas and N. A. D. Parlee, "On a Theory for the Deprivation of a Single Hard-Sphere Potential Describing the Overall Molecular Interactions in Binary Liquid Metal Alloys as a Function of Temperature and Composition", High Temperature Science 7, 259 (1975).

213. P. Protopapas and N. A. D. Parlee, "Theory of Transport in Liquid Metals. III. Calculation of Shear Viscosity Coefficients of Binary Alloys", Chemical Physics 11, 201 (1975).
214. A. S. Radtke and F. W. Dickson, "Carlinite,  $Tl_2S$ , A New Mineral from Nevada", Am. Mineralogist 60 (7-8), 559 (1975).
215. A. S. Radtke, C. M. Taylor, F. W. Dickson and C. Heropoulos, "Thallium-bearing Orpiment, Carlin Gold Deposit, Nevada", J. Research, U.S. Geol. Survey 2 (2), 341 (1974).
216. I. D. Raistrick and R. A. Huggins, "Considerations in the Use of Electrical Measurement Techniques to Evaluate Potential New Electrolytes and Mixed Conductors", Proc. Symp and Workshop on Advanced Battery Research and Design, Argonne National Laboratory (1976), p. B277.
217. I. Ramberg and A. M. Johnson, "A Theory of Concentric, Kink, and Sinusoidal Folding and of Monoclinial Flexuring of Compressible, Elastic Multilayers. Part V. Asymmetric Folding in Interbedded Chert and Shale of the Franciscan Assemblage, San Francisco Bay Area, California", Tectonophysics (1976).
218. Z. Reches and A. M. Johnson, "A Theory of Concentric, Kink, and Sinusoidal Folding and of Monoclinial Flexuring of Compressible, Elastic Multilayers. Part VI. Asymmetric Folding and Unidirectional Kinking", Tectonophysics (1976).
219. K. J. Reed, A. H. Zimmerman, H. C. Andersen and J. I. Brauman, "Cross Sections for Photodetachment of Electrons from Negative Ions Near Threshold", J. Chem. Phys. 64, 1368 (1976).
220. J. H. Richardson, L. M. Stephenson and J. I. Brauman, "Photodetachment of Electrons from Large Molecular Systems. Benzyl Anion. An Upper Limit to the Electron Affinity of  $C_6H_5CH_2$ ", J. Chem. Phys. 63, 74 (1975).
221. J. H. Richardson, L. M. Stephenson and J. I. Brauman, "Photodetachment of Electrons from Phenoxides and Thiophenoxide", J. Amer. Chem. Soc. 97, 2967 (1975).
222. \*B. Robinson, T. H. Geballe and J. M. Rowell, "Tunneling Study of Quench Condensed Superconducting Transition Metals", Bull. Am. Phys. Soc. 21, 402 (1976).
223. J. Rodine and A. M. Johnson, "The Ability of Debris, Heavily Freighted with Coarse Clastic Materials, to Flow on Gentle Slopes", Sedimentology 23, 213 (1976).
224. A. Rønnekleiv, H. J. Shaw and J. Souquet, "Grating Acoustic Scanners", Appl. Phys. Letts. 28 (7), 361 (1976).



225. A. Rønnekleiv, J. Souquet and H. J. Shaw, "Grating Acoustic Scanners", Ultrasonics Symp. Proc., p. 91 (1975).
226. °A. H. Ross and H. M. McConnell, "Permeation of a Spin-Label Phosphate into the Human Erythrocyte", Biochemistry 14 (13), 2793 (1975).
227. \*R. K. Route, R. S. Feigelson and R. J. Raymakers, "Elimination of Optical Scattering Defects in AgGaS<sub>2</sub> and AgGaSe<sub>2</sub>", J. Crystal Growth 33, 239 (1976).
228. \*S. Saha and W. C. Hayes, "Tensile Impact Properties of Human Compact Bone", J. Biomechanics 9, 243 (1976).
229. °J. Schoonman, L. B. Ebert, C.-H. Hsieh and R. A. Huggins, "Ionic Motion in  $\beta$ -PbF<sub>2</sub>", J. Appl. Phys. 46 (7), 2873 (1975).
230. °J. Schoonman and R. A. Huggins, "Composition Dependence of Ionic Conductivity", J. Phys. Chem. Solids 36, 815 (1975).
231. J. Schoonman and R. A. Huggins, "Electrical Properties of Undoped and Doped Potassium Tetrafluoroaluminate: KAlF<sub>4</sub>", J. Solid State Chem. 16, 413 (1976).
232. R. E. Schwall, G. R. Stewart and T. H. Geballe, "Low Temperature Specific Heat of Layered Compounds", J. Low Temp. Phys. 22, 557 (1976).
233. W. E. Seyfried, Jr., J. L. Bischoff and F. W. Dickson, "Basalt-seawater Interactions from 25°C-300°C and from 1-500 Bars: An Experimental Study", EOS Trans., Am. Geophysical Union 56 (12), 1073 (1975).
234. R. T.-S. Shiah and R. H. Bube, "Photoconductivity of Amorphous Compound Semiconductors Involving Elements from Groups IV, V and VI", J. Appl. Phys. 46 (5), 2005 (1976).
235. L. A. Sklar, B. S. Hudson and R. D. Simoni, "Conjugated Polyene Fatty Acids as Fluorescent Membrane Probes: Model System Studies", J. Supramolecular Structure 4, 449 (1976).
236. L. A. Sklar, B. S. Hudson and R. D. Simoni, "Conjugated Polyene Fatty Acids as Membrane Probes: Preliminary Characterization", Proc. Nat. Acad. Sci. USA 72, 1649 (1975).
237. R. Sokel and W. A. Harrison, "Long-Range Interactions in Semiconductors", Phys. Rev. Letts. 36, 5 (1976).
238. J. W. Spencer and A. Nur, "The Effects of Pressure Temperature and Pore Water on Velocities in Westerly Granite", J. Geophys. Res. 81, 899 (1976).

239. W. E. Spicer, "Bulk and Surface Ultraviolet Photoemission Spectroscopy", Chapter 12 in Optical Properties of Solids-New Developments, Ed. B. O. Seraphin, North-Holland Publishing Co., Amsterdam (1976), pp. 631-676.
240. W. E. Spicer, "Negative Affinity Photocathode Research and Technology", IEDM Digest 4.1, 57 (1975).
241. W. E. Spicer, P. W. Chye, P. E. Gregory, T. Sukegawa and I. A. Babalola, "Photoemission Studies of Surface and Interface States on III-V Compounds", J. Vac. Sci. Technol. 13, 233 (1976).
242. W. E. Spicer, P. E. Gregory, P. W. Chye, I. A. Babalola and T. Sukegawa, "Photoemission Study of the Formation of Schottky Barriers", Appl. Phys. Letts. 27, 617 (1975).
243. R. G. Stang, W. D. Nix and C. R. Barrett, "The Influence of Subgrain Boundaries on the Rate Controlling Creep Processes in Fe-3 Pct Si", Metallurgical Trans. A, 6A, 2065 (1975).
244. E. A. Stappaerts, "Harmonic Generation at High Field Strengths, Frequency Shifts and Saturation Phenomena", Phys. Rev. A 11, 1664 (1975).
245. C. Stein, S. Bouma, J. Carlson, C. Cornelius, J. Maeda, C. Weschler, F. A. Deutsch and K. O. Hodgson, "The Preparation and Structural Characterization of bis(2-mercaptoethylamine)ethylenediamine chromium (III) perchlorate", Inorg. Chem. 15, 1186 (1976).
246. T. Surek, J. P. Hirth and G. M. Pound, "The Screw Dislocation Spiral Mechanism of Crystal Growth and Evaporation", Proc. of the Soviet Academy of Sciences (USSR) 11, 203 (1975).
247. U. W. Suter and P. J. Flory, "Conformational Energy and Configurational Statistics of Polypropylene", Macromolecules 8, 765 (1975).
248. H. Taube, "Intramolecular Electron Transfer", Pure and Applied Chemistry 44, 1 (1975).
249. H. Taube and G. M. Tom, "The Mixed Valence Stated Based on  $\mu$ -Cyanogen-bis(pentaamineruthenium)", J. Amer. Chem. Soc. 97, 5310 (1975).
250. W. A. Tiller, "Kirlian Photography as an Electro-Therapeutics Research Tool", Int. J. of Acupuncture and Electro-Therapeutics Research (1976).
251. W. A. Tiller, "New Fields--New Laws", in Future Science, Eds. S. Krippner and J. White, Doubleday-Anchor (1976).

252. W. A. Tiller, "Present Scientific Understanding of the Kirlian Discharge Process", J. Osteopathic Physician (1976).
253. H. Topsøe, J. A. Dumesic and M. Boudart, "Catalytic and Magnetic Anisotropy of Iron Surfaces", in The Physical Basis for Heterogeneous Catalysis, Eds. E. Drauglis and R. I. Jaffee, Plenum Press, New York (1975), pp. 337-362.
254. C. H. Tsang, R. L. White and R. M. White, "Bloch, Neel and Head-to-Head Domain Wall Mobilities in  $\text{YFeO}_3$ ", 21st Annual Conference on Magnetism and Magnetic Materials, AIP Conference Proceedings 25 (1975).
255. J. van der Bosch and H. M. McConnell, "Fusion of Dipalmitoylphosphatidylcholine Vesicle Membranes Induced by Concanavalin A", Proc. Nat. Acad. Sci. USA 72 (11), 4409 (1975).
256. P. K. Vasudev, B. L. Mattes, E. Pietras and R. H. Bube, "Excess Capacitance and Non-Ideal Schottky Barriers on GaAs", Solid State Electronics 19, 557 (1976).
257. C. R. Wilson and H. Taube, "Acetate Complexes of Dirhodium and Diruthenium. Aquation and Reduction-Oxidation", Inorg. Chem. 14, 2276 (1975).
258. D. Y. Yoon and P. J. Flory, "Small Angle Neutron and X-ray Scattering by Poly(methyl methacrylate) Chains", Polymer 16, 645 (1975).
259. D. Y. Yoon and P. J. Flory, "II. Small-Angle Neutron and X-ray Scattering by Poly(methyl methacrylate) Chains", Macromolecules 9, 299 (1976).
260. D. Y. Yoon and P. J. Flory, "Small-Angle X-ray and Neutron Scattering by Polymethylene, Polyoxyethylene, and Polystyrene Chains", Macromolecules 9, 294 (1976).
261. D. Y. Yoon, P. R. Sundararajan and P. J. Flory, "Conformational Characteristics of Polystyrene", Macromolecules 8, 776 (1975).
262. D. Y. Yoon, U. W. Suter, P. R. Sundararajan and P. J. Flory, "Conformational Characteristics of Poly(methyl acrylate)", Macromolecules 8, 784 (1975).
263. C. M. Young, L. J. Anderson and O. D. Sherby, "Reply to 'On the Influence of the Mode of Deformation on the Hardening of Iron at Low Temperature and Large Strains'", Metallurgical Trans. A, 6A, 2164 (1975).
264. G. K. Youngren and A. Acrivos, "Rotational Friction Coefficients for Ellipsoids and Chemical Molecules with Slip Boundary Condition", J. Chem. Phys. 63, 3846 (1975).

265. K. Y. Yu, W. E. Spicer, I. Lindau, P. Pianetta and S. F. Lin,  
"Relationship of Heat of Chemisorption to  $\pi$ - and  $\sigma$ -Level Shifts  
as Measured by Photoemission", J. Vac. Sci. Technol. 13, 277 (1976).

## SECTION D

### DOCTORAL DISSERTATIONS

1. P. L. Adams, "Surface Acoustic Waveguides and Their Application to Optical Imaging Systems", Applied Physics (October 1975).
2. O. D. Ajayi, "Calculation of Motional Activation Enthalpy in Fast Ionic Conductors", Materials Science and Engineering (October 1975).
3. A. Albanese, "Mode Conversion in Anisotropic D Electric Optic Waveguides", Electrical Engineering (January 1976).
4. J. R. Anderson, "A New Model for Boron Diffusion in Silicon", Electrical Engineering (June 1976).
5. S. R. Aragon, "I. Dynamic Light Scattering from Macromolecules with Applications to Polydisperse Systems; II. Fluorescence Correlation Spectroscopy as a Probe of Molecular Dynamics", Chemistry (June 1976).
6. E. V. Auza, "The Diffusion of Nitrogen in Liquid Iron Alloys at 1600°C", Applied Earth Sciences (June 1976).
7. D. R. Bauer, "Depolarized Rayleigh Scattering Measurements of Rotational Motion of Small Molecules and Polymers", Chemistry (October 1975).
8. J. C. Bean, "Ion Implantation in Cadmium Telluride", Applied Physics (April 1976).
9. D. M. Bloom, "Optical Frequency Conversion in Metal Vapors", Electrical Engineering (October 1975).
10. S. P. Boughn, "I. The Interaction of Gravitational Waves with Matter; II. The Design and Construction of a Cryogenic Gravitational Wave Detector", Physics (October 1975).
11. R. W. Bradshaw, "Electrodiffusion in Polar Lipid Membranes of Molecular Dimensions", Chemical Engineering (April 1976).
12. P. Brûlet, "Magnetic Resonance Spectra of Membranes", Chemistry (October 1975).
13. C. W. Carlson, "Investigations on the Depolarized Rayleigh Scattering of Chain Molecules", Chemistry (January 1976).
14. R. L. S. Chang, "Permselectivity of the Glomerular Capillary Walls to Macromolecules", Chemical Engineering (October 1975).
15. K. Y. Cheng, "Preparation and Properties of  $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$  for Application to Luminescent Devices", Electrical Engineering (October 1975).

16. M. M. Choy, "Second Order Nonlinear Optical Processes in Semiconductors", Applied Physics (April 1976).
17. D. E. Claridge, "Nine Gigahertz Impedance Properties of Point-Contact Josephson Junctions", Physics (April 1976).
18. S. E. Diamond, "Functional Group Modifications Employing Ruthenium Ammines", Chemistry (October 1975).
19. W. E. Farneth, "I. The Mechanism of Isomerization of Bicyclo[2.1.0]pent-2-enes; II. Kinetic and Mechanistic Studies of Gas-Phase Proton-Transfer Reactions", Chemistry (October 1975).
20. S. A. Farnow, "Acoustic Applications of the Zone Plate", Applied Physics (January 1976).
21. R. N. Fleming, "The High Energy Broadly Tunable Coherent Source", Electrical Engineering (January 1976).
22. H. Gautier, "Acoustic Wave Semiconductor Convolver Applied to Electrical and Optical Signal Processing", Electrical Engineering (October 1975).
23. S. D. Gavazza, "Energy Release Rates and Associated Forces on Singular Dislocations", Applied Mechanics (October 1975).
24. P. E. Gregory, "Ultraviolet Photoemission Studies of the Surface States and Properties of the (110) Gallium Arsenide Surface, and of the Oxidation of Cesium", Electrical Engineering (January 1976).
25. M. T. Gür, "Electrochemical Reduction of Oxygen and Nitric Oxide on Stabilized Zirconia", Materials Science and Engineering (June 1976).
26. A. B. Hallak, "Superconductivity and Range of Existence of the A15 Phase in the Niobium-Germanium System", Physics (June 1976).
27. F. V. Hanson, "The Interaction of Hydrogen and Oxygen over Platinum Supported on Silica Gel Catalysts", Chemical Engineering (January 1976).
28. J. M. E. Harper, "Thermal Properties of Metals with Low Temperature Structural Instabilities", Applied Physics (October 1975).
29. H. H. Haung, "Mechanisms and Kinetics Study on Oxidative Roasting of Copper Concentrate--Lime Pellet", Applied Earth Sciences (January 1976).
30. J. H. Holbrook, "A Theoretical Investigation of Creep of Dispersion Strengthened Crystals", Materials Science and Engineering (June 1976).
31. E. G. Honea, "The Effect of Contact Strength on the Shape of Buckle Folds", Geology (January 1976).
32. H. S. Hwang, "The Interaction of Hydrogen with Small Palladium Crystallites", Chemical Engineering (January 1976).

33. T. J. Jach, "Observation of Nuclear Quadrupole Resonance with Superconducting Magnetometers", Physics (October 1975).
34. R. Joly, "Design of a Convolver for Optical Imaging", Electrical Engineering (June 1976).
35. M. E. Kaminsky, "Modulated Population Spectroscopy: Identification of Absorption Lines by Modulated Lower Level Population: Spectrum of the Diatomic Sodium Molecule", Physics (June 1976).
36. E. S. Kayali, "Superplasticity of Eutectoid Steel and Iron-Carbon Alloys", Materials Science and Engineering (June 1976).
37. B. T. Khuri-Yakub, "The Application of Zinc Oxide on Silicon to Surface Acoustic Wave Devices", Electrical Engineering (January 1976).
38. W. Kleeman, "Freeze-Fracture Studies of Protein-Lipid Interactions in Membranes", Chemistry (October 1975).
39. S. A. Lee, "Measurement of the Ground State Lamb Shift of Atomic Hydrogen and Deuterium by Laser Spectroscopy", Physics (January 1976).
40. D. B. Lidow, "Inelastic Collisions Induced by Intense Optical Radiation", Applied Physics (April 1976).
41. H. I. Lips, "Self-Diffusion in Liquids: Relation to Thermodynamic Properties and Effect of Strong Interactions", Chemical Engineering (October 1975).
42. C.-L. Lu, "Energy and Entropy Contributions to the Thermodynamic Properties of Liquid Metals", Chemical Engineering (January 1976).
43. R. W. Lund, "A Study of High Temperature Creep of Dispersion Strengthened Ni and Ni-20Cr", Materials Science and Engineering (January 1976).
44. K. S. Majumder, "The Structure and Properties of Alumina-Dispersed Copper Prepared by High Rate Physical Vapour Deposition", Materials Science and Engineering (June 1976).
45. W. H. McConnell, "Applications of Continuum Mechanics to Two Contemporary Problems in Materials Science", Mechanical Engineering (June 1976).
46. R. A. Meserve, "A Study of the Orbital Correction Method", Applied Physics (January 1976).
47. M. J. Mitchell, "Equilibrium Vapor Pressure Study of  $B_2S_3$  (Bismuothinite)", Applied Earth Sciences (January 1976).

48. J. Miyazaki, "Monte Carlo Calculation for the Determination of Surface Tension and Other Thermodynamic Properties of Simple Liquids", Materials Science and Engineering (January 1976).
49. M. R. Mruzik, "A Monte Carlo Study of Water and Ion-Water Clusters", Materials Science and Engineering (January 1976).
50. S. W. Mylroie, "Improved Range Statistics for Implanted Ions in Semiconductors", Electrical Engineering (October 1975).
51. G. A. Nystrom, "Combined Bounds Analysis of the Deformation of Plastic Structures Under Impact", Applied Mechanics (January 1976).
52. T. J. O'Leary, "Applications of Lasers to Chemical Problems", Chemistry (April 1976).
53. P. P. P. Pizzo, "An Investigation of the Effects of Precipitate Free Zones on the Mechanical Behavior of an Aluminum-Zinc-Magnesium Alloy", Materials Science and Engineering (January 1976).
54. M. D. Pocha, "High Voltage Double Diffusion MOS Transistors for Integrated Circuits", Electrical Engineering (April 1976).
55. R. M. Railey, "Computer Modeling of Proton Transfer Reactions at the Alumina/Water Interface", Applied Earth Sciences (January 1976).
56. K. J. Reed, "Electron Binding Energy and Electronic Charge Distribution in Negative Molecular Ions Determined by Photodetachment Spectroscopy", Chemistry (October 1975).
57. T. J. Rodgers, "Advanced Integrated Circuit Technology for Micro-power Integrated Circuits", Electrical Engineering (October 1975).
58. V. M. Sanjana, "Aspects of Membrane Transport in the Urinary Concentrating Mechanism", Chemical Engineering (October 1975).
59. D. C. Silverman, "A Study of the Surface Composition of Promoted Iron Catalysts by Auger Electron Spectroscopy", Chemical Engineering (January 1976).
60. E. A. Stappaerts, "Infrared Image Up-Conversion Alkali Metal Vapors", Electrical Engineering (June 1976).
61. R. A. Stark, "Sulfur-Containing Derivatives of a Rhodium Macrocycle", Chemistry (January 1976).
62. G. R. Stewart, "I. Size Effects in the Heat Capacity of Small Metal Particles; II. Heat Capacity of the Systems MnBi and MnSb", Applied Physics (October 1975).
63. L. J. Suter, "X-Ray Scattering from Liquid  $^3\text{He}$ ", Physics (April 1976).



64. D. D. Thomas, "Rotational Dynamics in Spin-Labeled Biomacromolecular Assemblies: Saturation Transfer Electron Paramagnetic Resonance", Biophysics (January 1976).
65. G. M. Tom, "Chemistry of Mixed Valence Binuclear and Polynuclear Ruthenium Complexes", Chemistry (October 1975).
66. R. E. Tremain, Jr., "Doping Gallium Arsenide by Ion Implantation and Proton-Enhanced Diffusion", Electrical Engineering (April 1976).
67. J. P. Wikswo, Jr., "Non-Invasive Magnetic Measurement of the Electrical and Mechanical Activity of the Heart", Physics (January 1976).
68. E. G. Wilson, "Local and Nonlocal Effects in the Penetration of Magnetic Fields into Superconducting Tin Film Cylinders", Physics (June 1976).
69. P. W. Worden, Jr., "A Cryogenic Test of the Equivalence Principle", Physics (April 1976).
70. R. W. Young, "Thermomechanical Coupling Effects in the Deformation of Viscoelastic Solids", Applied Mechanics (October 1975).
71. G. K. Youngren, "Some Laminar Flow Problems at Small and Moderate Reynolds Numbers: Numerical Solutions and Experiments", Chemical Engineering (October 1975).
72. K. K. Y. Yu, "Photoemission and Thermal Desorption Studies of the Adsorption of Simple Molecules on Transition Metals and Alloys", Electrical Engineering (June 1976).

# APPENDIX - I

## I. FACULTY MEMBERS PARTICIPATING IN MATERIALS RESEARCH

Name	Title	Department(s)
A. Acrivos	Professor	Chemical Engineering
H. C. Andersen	Assoc. Professor	Chemistry
R. N. Anderson	Assoc. Professor	Applied Earth Sciences
B. A. Auld	Adjunct Professor	Hansen Laboratories
*D. M. Barnett	Assoc. Professor	Materials Science & Engineering, Mechanical Engineering
°C. R. Barrett	Assoc. Professor	Materials Science & Engineering
C. W. Bates, Jr.	Assoc. Professor	Materials Science & Engineering, Electrical Engineering
M. R. Beasley	Assoc. Professor	Applied Physics, Electrical Engineering
A. I. Bienenstock	Professor	Materials Science & Engineering, Applied Physics
M. Boudart	Professor	Chemical Engineering, Chemistry
J. I. Brauman	Professor	Chemistry
G. E. Brown	Asst. Professor	Geology
R. H. Bube	Professor	Materials Science & Engineering, Electrical Engineering
R. L. Byer	Assoc. Professor	Applied Physics
*J. P. Collman	Professor	Chemistry
T. J. Connolly	Professor	Mechanical Engineering
+F. W. Dickson	Professor of Geochemistry	Geology
+S. Doniach	Professor	Applied Physics
R. H. Eustis	Professor	Mechanical Engineering
C. W. F. Everitt	Adjunct Professor	Hansen Laboratories
+W. M. Fairbank	Professor	Physics

\*CMR Executive Committee Member

+On Leave During Academic Year

°Left Stanford December 1975

M. D. Fayer	Asst. Professor	Chemistry
+P. J. Flory	Professor Emeritus	Chemistry
H. O. Fuchs	Professor Emeritus	Mechanical Engineering
*T. H. Geballe	Professor	Applied Physics, Materials Science & Engineering
J. F. Gibbons	Professor	Electrical Engineering
R. P. Giffard	Asst. Professor	Physics
S. S. Hanna	Professor	Physics
T. W. Hänsch	Assoc. Professor	Physics
S. E. Harris	Professor	Electrical Engineering
+W. A. Harrison	Professor	Applied Physics
W. C. Hayes	Asst. Professor	Applied Mechanics, Surgery
G. Herrmann	Professor	Mechanical Engineering, Civil Engineering
K. O. Hodgson	Asst. Professor	Chemistry
B. S. Hudson	Asst. Professor	Chemistry
*R. A. Huggins	Professor	Materials Science & Engineering
A. M. Johnson	Assoc. Professor	Geology, Applied Earth Sciences
J. D. Khazzoom	Visiting Professor	Operations Research
G. S. Kino	Professor	Electrical Engineering
C. H. Kruger	Professor	Mechanical Engineering
E. H. Lee	Professor	Mechanical Engineering, Aeronautics & Astronautics
J. E. Lind, Jr.	Assoc. Professor	Chemical Engineering
E. I. Lindau	Adjunct Professor	Electrical Engineering
+*W. A. Little	Professor	Physics
+W. C. Luth	Assoc. Professor	Geology
R. J. Madix	Assoc. Professor	Chemical Engineering
R. L. Mallett	Asst. Professor	Applied Mechanics
D. M. Mason	Professor	Chemical Engineering, Chemistry
H. M. McConnell	Professor	Chemistry
J. D. Meindl	Professor	Electrical Engineering
D. A. Nagel, M.D.	Professor	Orthopaedic Surgery
W. D. Nix	Professor	Materials Science & Engineering

A. M. Nur	Assoc. Professor	Geophysics
R. H. Pantell	Professor	Electrical Engineering
G. A. Parks	Professor	Applied Earth Sciences, Geology, Civil Engineering
N. A. D. Parlee	Professor of Metallurgy	Applied Earth Sciences
+*G. L. Pearson	Professor Emeritus	Electrical Engineering
R. Pecora	Assoc. Professor	Chemistry
R. L. Piziali	Asst. Professor	Mechanical Engineering
G. M. Pound	Professor	Materials Science & Engineering
C. F. Quate	Professor	Applied Physics, Electrical Engineering
C. W. Richards	Professor	Civil Engineering
C. R. Robertson	Assoc. Professor	Chemical Engineering
A. L. Schawlow	Professor	Physics
D. J. Schurman, M.D.	Asst. Professor	Orthopaedic Surgery
H. A. Schwettman	Professor	Physics
S. A. Self	Adjunct Professor	Mechanical Engineering
H. J. Shaw	Adjunct Professor	Hansen Laboratories
O. D. Sherby	Professor	Materials Science & Engineering
+J. C. Shyne	Professor	Materials Science & Engineering
A. E. Siegman	Professor	Electrical Engineering
*W. E. Spicer	Professor	Electrical Engineering, Materials Science & Engineering
*D. A. Stevenson	Professor	Materials Science & Engineering
H. Taube	Professor	Chemistry
W. A. Tiller	Professor	Materials Science & Engineering
B. B. Triplett	Asst. Professor	Physics
M. Weissbluth	Assoc. Professor	Applied Physics
R. L. White	Professor	Electrical Engineering, Materials Science & Engineering
J. F. Young	Adjunct Professor	Electrical Engineering

## APPENDIX - II

### II. RESEARCH ASSOCIATES AND PROFESSIONAL STAFF

A. Abe	Chemistry
J. T. Anderson	Hansen Laboratories
T. W. Barbee, Jr.	Center for Materials Research
C. W. Beer, Jr.	Chemistry
M. Belombe	Physics
J. E. Benson	Chemical Engineering
J. L. Bischoff	Geology
D. M. Bloom	Electrical Engineering
W. L. Bond	Hansen Laboratories
S. P. Boughn	Physics
B. A. Boukamp	Materials Science & Engineering
D. P. Boyd	Hansen Laboratories
G. Brown	Chemistry
P. Brulet	Chemistry
B. Cabrera	Physics
P. H. Ceperley	Hansen Laboratories
V. K. Cheng	Physics
S. Ciraci	Materials Science & Engineering
J. M. Criado	Chemical Engineering
R. Dalla Betta	Chemical Engineering
R. C. DeMattei	Center for Materials Research
L. R. Elias	Hansen Laboratories
A. G. Elliot	Materials Science & Engineering
C. M. Elliott	Chemistry
D. Elwell	Center for Materials Research
N. Endow	Center for Materials Research
A. L. Fahrenbruch	Materials Science & Engineering
R. S. Feigelson	Center for Materials Research
P. M. Fenn	Geology
E. Fortin	Electrical Engineering
D. Franco	Chemistry
A. L. Frennet	Chemical Engineering
J. Goodfellow	Chemistry
H. R. Greenstein	Materials Science & Engineering
P. E. Gregory	Electrical Engineering
H. Gutfreund	Physics
R. H. Hammond	Hansen Laboratories
J. B. Hastings	Materials Science & Engineering
G. B. Haydon	Center for Materials Research
S. E. Hayes	Chemistry

R. L. Herbst	Applied Physics
R. E. Howard	Hansen Laboratories
G. M. K. Humphries	Chemistry
G. Ilonca	Materials Science & Engineering
H. Ito	Geophysics
H. C. Jain	Physics
C. F. Jako	Materials Science & Engineering
J. S. Johannessen	Electrical Engineering
B. T. Khuri-Yakub	Hansen Laboratories
D. L. Keith	Center for Materials Research
C. N. King	Applied Physics
R. A. Klemm	Hansen Laboratories
I. Knyazev	Physics
R. Koch	Center for Materials Research
J. K. Koester	Mechanical Engineering
E. L. Kugler	Chemical Engineering
J. W. Kung	Chemistry
P. G. Kury	Chemistry
B. N. Kuznetsov	Chemistry
G. Langouche	Physics
Q.-H. Lao	Chemistry
D. B. Leiser	Materials Science & Engineering
J. T. Lewis	Chemistry
G. C. Li	Hansen Laboratories
J. A. Lipa	Hansen Laboratories
J. M. Lockhart	Physics
R. Lorentz	Physics
A. Lu	Chemistry
C. M. Lyneis	Hansen Laboratories
J. M. Madey	Hansen Laboratories
J. Malmivuo	Physics
J. E. Mark	Chemistry
B. L. Mattes	Center for Materials Research
M. S. McAshan	Hansen Laboratories
A. K. Miller	Materials Science & Engineering
T. Minamisono	Physics
M. J. Mottl	Geology
J. Murdock	Chemistry
M. Mutter	Chemistry
L. E. Nagel	Materials Science & Engineering

D. H. Napper	Chemistry
H. Neidlinger	Chemistry
C. H. C. New	Physics
G. Nord	Chemistry
H. J. Paik	Hansen Laboratories
G. I. Panov	Chemical Engineering
M. A. Piestrup	Electrical Engineering
K. R. Pisharody	Hansen Laboratories
J. D. Plummer	Electrical Engineering
R. A. Powell	Electrical Engineering
L. Price	Geology
M. K. Pyzyna	Center for Materials Research
A. S. Radtke	Geology
I. D. Raistrick	Materials Science & Engineering
D. Ramsey	Physics
P. Rey	Chemistry
K. Rieder	Chemistry
E. P. Rose	Chemistry
F. M. Rose	Chemistry
G. B. Rothbart	Applied Physics
R. K. Route	Center for Materials Research
S. C. Rowland	Materials Science & Engineering
E. Saiz	Chemistry
K. C. Saraswat	Electrical Engineering
T. K. Saylor	Physics
G. Schmuckler	Chemistry
T. I. Smith	Hansen Laboratories
G. R. Stewart	Center for Materials Research
H. Sunada	Materials Science & Engineering
U. W. Suter	Chemistry
E. H. Z. Taheri	Materials Science & Engineering
B. S. Tovrog	Chemistry
J. P. Turneure	Hansen Laboratories
J. Van der Bosch	Chemistry
F. J. VanKann	Hansen Laboratories
J. D. Vine	Geology
A. von Kameke	Chemistry
J. Wadsworth	Materials Science & Engineering
A. Waleh	Chemistry
R. Wallenstein	Hansen Laboratories

T. M. Waugh	Hansen Laboratories
J. Weiss	Chemistry
W. Weppner	Materials Science & Engineering
R. Whalen	Materials Science & Engineering
J. P. Wikswo, Jr.	Physics
D. K. Winslow	Hansen Laboratories
F. C. Witteborn	Physics
A. Wlodawer	Chemistry
C. P. Wong	Chemistry
P. W. Worden, Jr.	Physics
C. Yeh	Electrical Engineering
W. M. Yen	Physics
S. Yoshida	Chemical Engineering
C. R. Zercher	Center for Materials Research
L. T. Zitelli	Hansen Laboratories
J. Zittartz	Hansen Laboratories
I. V. Zubeck	Center for Materials Research
R. B. Zubeck	Hansen Laboratories



## APPENDIX - III

### III. GRADUATE STUDENTS PARTICIPATING IN MATERIALS RESEARCH PROGRAMS

#### APPLIED EARTH SCIENCES

K. W. Aul	H.-H. Haung	R. M. Railey
E. V. Auza	G. R. Holzhausen	J. L. Renner
N. Bakshani	J.-H. Hou	S. Savcioglu
R. L. Bassett	J. R. Hwang	A. E. Soto
G. E. Beckstead	A. Jayarajan	Z. Tekneci
T.-H. Chin	K. D. Keefer	R. W. Turnbull
B. H. Coyle, Jr.	W.-Y. Lim	D. M. Yadon
R. P. Ebro	L. J. McAllister	

#### APPLIED PHYSICS

K. N. Bates	S. H. Hunter	P. A. Pianetta
J. C. Bean	G. R. Ierley	E. H. Rezayi
P. G. Borden	D. B. Kimhi	S. T. Ruggiero
H. C. Brayman	H. Komine	A. M. Salau
S. J. Brosnan	W. P. Leung	D. H. Smith
K. A. Buzard	J. I. Levatter	R. J. Sokel
M. M. Choy	A. Lidow	G. R. Stewart
P. W. Chye	D. B. Lidow	R. A. Thomas
S. R. Early	J. W. McKenzie	L. A. Turkevich
S. A. Farnow	D. K. Misemer	R. B. van Dover
J. D. Fraser	D. F. Moore	G. O. White
J. M. Harper	R. H. Norton	J. C. White
G. A. Hayward	Y. Park	D. C. Wolfe
M. A. Henesian	G. A. Pavlath	M. D. Wright
R. E. Howard	D. W. Pettibone	G. A. Zdasiuk
K. S. Hsu	J. C. Phillips	P. Zorabedian
Y. W. Hu		

#### GEOLOGY

B. G. Aitken	J. L. Krumhansl	Z. Reches
A. Aydin	B. A. Mills	J. J. Rytuba
J. A. Baltierra	J. P. Murray	D. H. Scofield
B. H. W. S. de Jong	M. T. Naney	M. P. Taylor
W. E. Dibble, Jr.	J. D. O'Brient	C. H. Trautmann
J. H. Fink	J. A. Peterson	

## CHEMICAL ENGINEERING

N. M. Abbas	D. S. Inloes	D. J. O'Rear
B. L. Beegle	S. W. Johnson	V. M. Sanjana
M. P. Bohrer	S. Ladas	I.-S. Shaw
R. W. Bradshaw	K. J. Lim	D. C. Silverman
R. L. S. Chang	H. I. Lips	I. E. Wachs
J. C. Chapman	T. S. Lo	R. W. Watkins
H.-S. Chen	B. K. Lok	C. J. Wen
F. A. Gadala-Maria	C.-L. Lu	M. Yamada
G. L. Gussis	C. L. M. McConica	D. H. S. Ying
F. V. Hanson	S. R. Moosman	G. K. Youngren
H. S. Hwang	D. Y. Ngan	

## CHEMISTRY

J. R. Andrews	C. R. Gochanour	R. N. Rosenfeld
S. R. Aragon	R. Gooden	A. H. Ross
O. I. Asubiojo	S. E. Groh	R. K. Rothrock
D. R. Bauer	T. R. Halbert	N. E. Schlotter
J. O. Bjarnason	W. M. Hetherington	E. R. Schmittou
W. A. Boettner	R. E. Jacobs	M. A. Schwartz
S. E. Bott	B. K. Janousek	S. K. Seidel
J. D. Buhr	H. A. Karp	J. P. Sen
C. W. Carlson	H. J. Krentzien	J. R. Sheats
P. A. Christian	F. W. Kutzler	L. A. Sklar
D. E. Cooper	Y.-L. Lam	T. N. Sorrell
B. R. Copeland	T. Lewis	S. G. Stanton
C. W. Cornelius	E. J. Luna	R. A. Stark
S. P. Cramer	A. M. Madonik	C. A. Stein
J. H. Dawson	M. L. Marrocco	K. S. Suslick
L. C. DeBolt	P. L. Matlock	J. E. Sutton
P. Denisevich, Jr.	H. L. McPeters	D. D. Walker
J. J. Diamond	L. P. Miller	R. P. Walker
D. D. Dlott	M. L. Murtiff	R. S. Webber
T. K. Eccles	M. K. Neuberg	R. D. Wieting
W. E. Farneth	T. J. O'Leary	M. A. Willia
R. G. Finke	W. N. Olmstead	P. K. Wolber
M. R. Gilberg	K. J. Reed	A. H. Zimmerman

### ELECTRICAL ENGINEERING

A. Albanese	R. N. Fleming	H. Park
E. Ammar	A. Gat	M. D. Pocha
J. R. Anderson	W. R. Green	R. L. Reif-G
H. J. Arditty	P. E. Gregory	J. R. Salcedo
A. Atalar	M. A. Hall	B. W. Scharf
R. A. Baumgartner	T. Hermann	C. C. Shen
G. W. Bekkers	C. P. H. Ho	Y. D. Shen
D. G. Boyers	Y.-M. Houg	J. Souquet
L. N. Bui	K. G. Jew	E. A. Stappaerts
K.-I. Chang	V. B. Jipson	P. M. Stefan
C.-K. Chen	R. Joly	R. E. Tremain, Jr.
C.-H. Cheng	J.-S. Kim	C. H. Tsang
K. Y. Cheng	M. R. Kump	H. C. Tuan
A. Chu	D. T. Ling	S. Warshaw
A. N. Chu	J. C. Mein	F. C. Wu
D. M. Collins	J. N. Miller	E. M. Young
C. S. Desilets	S. W. Mylroie	R. G. Younge
A. J. Duerinckx	J. H. Newton	K. K. Y. Yu
R. W. Falcone		

### MATERIALS SCIENCE AND ENGINEERING

O. B. Ajayi	N. A. Godshall	J. T. Lo
J. Aranovich	S. H. Goods	R. W. Lund
F. L. Banta	M. T. Gur	Y. Y. Ma
F. Buch	D. J. HaferBurns	J. E. Mahan
M. A. Burke	S. Hahn	K. S. Majumder
R. D. Caligiuri	W. G. Haines	R. L. Marantz
S.-H. S. Chiao	M. S. Hassan	A. E. McHale
B. A. Chin	E. E. Hellstrom	G. M. Michal
R. Chow	C. Ho	K. W. Mitchell
M. Chu	J. H. Holbrook	J. Miyazaki
U. Cohen	O. L. Hsu	D. N. Modlin
D. Das-Gupta	Z. S. Jan	M. R. Mruzik
H. Dun	F. Q. Johnson	G. M. Pharr
L. E. Eiselstein	E. D. Jones	H. D. Rodeen
C. V. H. Fuchs	E. S. Kayali	J. R. Salem
K. P. Fuchs	R. H. Klundt	C. G. Schmidt
L. Galan	J. E. Leiss	G. S. Selvaduray
C. M. Garner	B. E. Liebert	C.-J. Shih
J. C. Gibeling	J.-H. Lin	M. Shimizu
P. S. Gilman	S.-M. Liu	J. G. Slater

## MATERIALS SCIENCE AND ENGINEERING (Continued)

J. W. Sliwa, Jr.	H. A. Vander Plas	R. A. White
J. R. Spingarn	K. P. Vasudev	T. M. Wright
M. E. Thomas	R. G. Walmsley	M. C. Wu
N.-H. Tsai	C. J. Wei	B. P. J. Yen

## MECHANICAL ENGINEERING

P. C. Ariessohn	M. K. Jenkins	D. C. Rastegar
V. G. Baghdasarians	W. H. McConnell	M. E. Rodgers
D. R. Carter	D. V. Nelson	W. P. Seering
T. J. Delph	R. M. Nelson	F. Tanner
K. A. Derbalian	G. A. Nystrom	A. Velez-Covo
S. D. Gavazza	E. M. Olsen	T. B. Wertheimer
L. C. Hsu	S. T. Olson	R. W. Young
J. B. C. Hunter		

## PHYSICS

J. W. Brill	M. E. Kaminsky	J. S. Philo
S. P. Boughn	S. Kim	B. Robinson
D. E. Claridge	F. V. Kowalski	R. A. Sears
D. A. Deacon	G. S. LaRue	J. H. Stanley
N. S. Dixon	S. M. Lazarus	M. A. Taber
J. N. Eckstein	S. A. Lee	R. E. Teets
R. Feinberg	W. A. Little	A. M. Vetter, Jr.
J. N. Fields	J. M. Lockhart	C. A. Waters
J. E. Goldsmith	D. M. Lublin	G. A. Westenskow
J. R. Hall	Y. A. Mahmud	C. E. Wieman
A. B. Hallak	P. L. Marston	J. P. Wikswo, Jr.
R. T. Hawkins	P. F. Michelson	E. G. Wilson
J. N. Hollenhorst	B. J. Neuhauser	P. W. Worden, Jr.
J. W. Hugg	M. A. Novotny	C. H.-C. Yuen
T. J. Jach	M. C. O'Conner	L. J. Zych
D. Jackson	T. P. Orlando	

## OTHER DEPARTMENTS

### BIOPHYSICS

D. D. Thomas

### CIVIL ENGINEERING

D. A. Burciaga  
A. Kerdegari

### GEOPHYSICS

M. L. Bell	S. L. McHugh
R. P. Denlinger	M. A. Spieth
M. A. Grosenbaugh	E. S. Sprunt
K. D. Mahrer	S. C. Wang
G. M. Mavko	J. D. Weeks

# APPENDIX - IV

## IV. GRADUATE DEGREES CONFERRED

### Doctor of Philosophy

---

P. L. Adams	Applied Physics
O. B. Ajayi	Materials Science and Engineering
A. Albanese	Electrical Engineering
J. R. Anderson	Electrical Engineering
S. R. Aragon	Chemistry
E. V. Auza	Applied Earth Sciences
D. R. Bauer	Chemistry
J. C. Bean	Applied Physics
D. M. Bloom	Electrical Engineering
S. P. Boughn	Physics
R. W. Bradshaw	Chemical Engineering
P. Brulet	Chemistry
C. W. Carlson	Chemistry
R. L. S. Chang	Chemical Engineering
K. Y. Cheng	Electrical Engineering
M. M. Choy	Applied Physics
D. E. Claridge	Physics
S. E. Diamond	Chemistry
W. E. Farneth	Chemistry
S. A. Farnow	Applied Physics
R. N. Fleming	Electrical Engineering
H. R. Gautier	Electrical Engineering
S. D. Gavazza	Applied Mechanics
P. E. Gregory	Electrical Engineering
M. T. Gür	Materials Science & Engineering
A. B. Hallak	Physics
F. V. Hanson	Chemical Engineering
J. M. Harper	Applied Physics
H.-H. Haung	Applied Earth Sciences
J. H. Holbrook	Materials Science and Engineering
E. G. Honea	Geology
H. S. Hwang	Chemical Engineering
T. J. Jach	Physics
R. Joly	Electrical Engineering
M. E. Kaminsky	Physics
E. S. Kayali	Materials Science and Engineering
B. T. Khuri-Yakub	Electrical Engineering
W. Kleemann	Chemistry
S. A. Lee	Physics
D. B. Lidow	Applied Physics

# GRADUATE DEGREES CONFERRED

## Doctor of Philosophy (Continued)

---

H. I. Lips	Chemical Engineering
C.-L. Lu	Chemical Engineering
R. W. Lund	Materials Science and Engineering
K. S. Majumder	Materials Science and Engineering
W. H. McConnell	Mechanical Engineering
R. A. Meserve	Applied Physics
M. J. Mitchell	Applied Earth Sciences
J. Miyazaki	Materials Science and Engineering
M. R. Mruzik	Materials Science and Engineering
S. W. Mylroie	Electrical Engineering
G. A. Nystrom	Applied Mechanics
T. J. O'Leary	Chemistry
P. P. Pizzo	Materials Science and Engineering
M. D. Pocha	Electrical Engineering
R. M. Railey	Applied Earth Sciences
K. J. Reed	Chemistry
T. J. Rodgers	Electrical Engineering
V. M. Sanjana	Chemical Engineering
D. C. Silverman	Chemical Engineering
E. A. Stappaerts	Electrical Engineering
R. A. Stark	Chemistry
G. R. Stewart	Applied Physics
L. J. Suter	Physics
D. D. Thomas	Biophysics
G. M. Tom	Chemistry
R. E. Tremain, Jr.	Electrical Engineering
J. P. Wikswo, Jr.	Physics
E. G. Wilson	Physics
P. W. Worden, Jr.	Physics
R. W. Young	Applied Mechanics
G. K. Youngren	Chemical Engineering
K. K. Y. Yu	Electrical Engineering

## Engineer

---

B. H. Coyle, Jr.	Applied Earth Sciences
A. Kerdegari	Civil Engineering
S. Warshaw	Electrical Engineering

# GRADUATE DEGREES CONFERRED

## Master of Science

---

P. C. Ariessohn	Mechanical Engineering
A. Atalar	Electrical Engineering
K. W. Au	Applied Earth Sciences
J. W. Brill	Physics
F. L. Banta	Materials Science and Engineering
S. M. Eston	Applied Earth Sciences
L. E. Eiselstein	Materials Science and Engineering
C. V. H. Fuchs	Materials Science and Engineering
K. P. Fuchs	Materials Science and Engineering
J. C. Gibeling	Materials Science and Engineering
J. E. Goldsmith	Physics
S. H. Goods	Materials Science and Engineering
D. J. HaferBurns	Materials Science and Engineering
W. G. Haines	Materials Science and Engineering
R. S. Hanni	Physics
R. T. Hawkins	Physics
J. W. Hugg	Physics
M. K. Jenkins	Mechanical Engineering
V. B. Jipson	Electrical Engineering
F. Q. Johnson	Materials Science and Engineering
S. Ladas	Chemical Engineering
J. E. Mahan	Materials Science and Engineering
R. L. Marantz	Materials Science and Engineering
C. L. M. McConica	Chemical Engineering
A. E. McHale	Materials Science and Engineering
S. L. McHugh	Materials Science and Engineering
J. N. Miller	Electrical Engineering
L. P. Miller	Chemistry
R. A. Mills	Electrical Engineering
D. F. Moore	Applied Physics
J. A. Peterson	Geology
D. W. Pettibone	Applied Physics
D. K. Riley	Geophysics
D. H. Scofield	Geology
G. S. Selvaduray	Materials Science and Engineering
I.-S. Shaw	Chemical Engineering
P. M. Stefan	Electrical Engineering
M. E. Thomas	Materials Science and Engineering
C. H. Trautmann	Geology
R. G. Walmsley	Materials Science and Engineering

## GRADUATE DEGREES CONFERRED

### Master of Science (Continued)

---

T. B. Wertheimer	Applied Mechanics
J. C. White	Applied Physics
M. D. Wright	Applied Physics
M. Yamada	Chemical Engineering
C. H.-C. Yuen	Physics
P. Zorabedian	Applied Physics



# V. NAME INDEX

Aaronson, H. I.  
C\*-346\*\*

Abbas, N. M.  
B-198

Abe, A.  
B-113

Abraham, F. F.  
C-346,360

Acrivios, A.  
B-3  
C-361,365

Adams, P. L.  
C-346  
D-367

Aitkin, B. G.  
B-53

Ajayi, O. B.  
B-177  
C-346  
D-367

Albanese, A.  
B-272  
D-367

Amirnazmi, A.  
C-346

Ammar, E.  
B-126

Andersen, H. C.  
B-245  
C-356,361,362

Anderson, J. R.  
B-126  
D-367

Anderson, J. T.  
B-86

Anderson, L. J.  
C-365

Anderson, R. N.  
B-5,245  
C-346,351,354,  
357

Andrews, J. R.  
B-170

Aragon, S. R.  
B-49,260  
C-346  
D-367

Aranovich, J.  
B-60

Arditty, H.  
B-282

Ariessohn, P. C.  
B-84

Asubiojo, O. I.  
B-49  
C-346

Atalar, A.  
B-272

Attal, J.  
C-346

Au, K. W.  
B-245

Auld, B. A.  
B-10  
C-353

Auza, E.  
B-245  
D-367

Babalola, I. A.  
C-350,364

Baghdasarians, V.  
B-117

Bakshani, N.  
B-245

Barbee, T. W., Jr.  
B-14,119,122

Barker, J. A.  
C-360

Barnett, D. M.  
B-25,236  
C-346,347,354,  
359

Barrett, C. R.  
B-14  
C-364

Bassett, R. L.  
B-241

Bates, C. W., Jr.  
B-29  
C-347,353

Bates, K. N.  
B-282

Batra, I. P.  
C-350

Bauer, D. R.  
B-49,260  
C-347  
D-367

\*Section Numbers  
\*\*Page Numbers

B - Programs  
C - Publications  
D - Doctoral Dissertations

Baumgartner, R. B-69	Bloom, D. M. B-150 C-347 D-367	Brauman, J. I. B-49 C-346,347,348, 350,352,362
Bean, J. C. B-126 D-367	Blount, G. H. C-348	Brayman, H. C. B-297
Beasley, M. R. B-14,38,119 C-357,360	Boettner, W. A. B-113	Breiland, W. G. C-348
Beckstead, G. E. B-5	Bohrer, M. P. B-275	Brenner, H. C. C-348
Beegle, B. L. B-45	Bond, W. L. B-282 C-348	Brill, J. W. B-194
Bekkers, G. W. B-150 C-347	Boolchand, P. B-132	Brock, J. C. C-348
Bell, M. L. B-236	Borden, P. G. B-181	Brosnan, S. B-69
Belombe, M. B-194	Bott, S. E. B-260	Brown, G. B-331
Benson, J. E. B-45	Boudart, M. B-14,45 C-346,348,351, 352,353,365	Brown, G. E. B-53 C-348,351,352, 353
Bienenstock, A. I. B-14,41 C-347,354,356	Boughn, S. P. B-86 D-367	Brulet, P. B-209 C-348 D-367
Bilir, N. C-347	Boukamp, B. B-177	Bube, R. H. B-60,203 C-348,349,353 358,360,363, 365
Bischoff, J. L. B-77 C-363	Bouma, S. C-364	Buch, F. B-60 C-349,353
Bjarnason, J. B-170	Boyd, D. P. B-86	Bucher, E. B-132
Bjorklund, G. C. C-347	Boyers, D. G. B-335	Budiansky, B. C-357
Blair, L. K. C-347	Bradshaw, R. W. B-275 D-367	

Buhr, J. D. B-331	Chabay, I. C-350	Christian, P. A. B-72 C-350
Bui, L. N. B-282	Chadi, D. J. C-350	Chu, A. N. B-238
Bunnenberg, E. C-351	Chang, K. I. B-254	Chu, C. W. C-350
Burciaga, D. A. B-274	Chang, R. L. S. B-275 D-367	Chu, M. B-60
Burke, M. A. B-219 C-349	Chang, V. W. C. C-353	Chye, P. W. B-303 C-350,354,364
Burland, D. C-351	Chapman, J. C. B-203	Ciraci, S. B-335 C-350
Byer, R. L. B-69 C-349,355,357	Chen, C. K. B-238 C-361	Claridge, D. E. B-86 D-368
Cabrera, B. B-86	Chen, H.-S. B-3 C-355	Cohen, U. B-177 C-350
Caligiuri, R. B-288 C-349	Cheng, C. H. B-29	Coldren, L. A. C-350
Carlson, C. W. B-113 D-367	Cheng, K. Y. B-254 D-367	Collins, D. M. B-303 C-350
Carlson, J. C-364	Chiao, S.-H. B-60,205	Collman, J. P. B-72 C-350,351
Carter, C. A. C-349	Chin, B. A. B-260	Connolly, T. J. B-5
Carter, D. R. B-158 C-349,354	Chin, T. H. B-5	Conrad, J. C. C-351
Casey, H. C., Jr. C-349	Chow, K. T. C-353	Cooper, D. E. B-99
Ceperley, P. H. B-86	Chow, R. B-335	Copeland, B. R. B-209
	Choy, M. M. B-69 D-368	

Cornelius, C. W. B-49,260 C-364	DeMattei, R. C. B-105 C-353	Djerassi, C. C-351
Coyle, B. H. B-5 C-351	Denisevich, P. B-72 C-350	Dlott, D. D. B-99 C-352
Cramer, S. P. B-164,170 C-351	Denlinger, R. P. B-232	Dodd, R. T. C-352
Criado, J. M. B-45	Depoy, P. E. C-359	Doniach, S. B-80 C-351,352
Cubicciotti, D. B-5	Derbalian, K. A. B-186	Drucker, D. C. C-357
Current, S. C-350	Derouane, E. G. C-348	Duerinckx, A. J. B-297
Cutler, C. C. C-348	DeSilets, C. S. B-181 C-352,357	Dumesic, J. A. C-348,352,365
Dalla Betta, R. A. B-45 C-351	Deutsch, F. A. C-364	Dun, H. B-205,323
Das-Gupta, D. B-29	Diamond, J. J. B-170 C-353,355	Dunitz, J. D. C-355,357
Dawson, J. H. B-170 C-350	Diamond, S. E. C-352 D-368	Early, S. R. B-122 C-350
Deacon, D. A. B-86	Dibble, W. E. B-77,335	Ebert, L. B. C-352,363
DeBolt, L. C. B-113	Dickson, F. W. B-77 C-362,363	Ebro, R. P. B-241
deJong, B. H. W. S. B-53 C-351	DiMelfi, R. J. C-352	Eccles, T. K. B-164 C-349,351
Delbouille, A. C-348	DiSalvo, F. J. C-354	Eckert, C. A. B-5
Delph, T. B-161	Dixon, N. S. B-132	Eckstein, J. B-276
		Edwards, G. R. C-352,356

Eiselstein, L. B-288	Farnow, S. A. B-10 C-353 D-368	Fraser, J. D. B-181 B-352,353,357
Elias, L. R. B-86 C-352	Fayer, M. D. B-99 C-348,352,353	Frennet, A. B-45
Elliot, A. G. B-177,205 C-353	Feigelson, R. S. B-105,177,205 C-353,363	Freund, L. B. B-236 C-347
Elliott, C. M. B-72,323	Feinberg, R. B-276	Fripiat, J. G. C-353
Elwell, D. B-177 C-353	Fenn, P. M. B-53,196 C-348,353	Fuchs, C. V. H. B-177
Endow, N. B-177	Fields, J. N. B-80	Fuchs, H. O. B-117
Eschenmosher, A. C-357	Finke, R. G. B-72	Fuchs, K. P. B-219
Eustis, R. H. B-84	Fleming, R. N. B-69 D-368	Fuwa, A. C-354
Everitt, C. W. F. B-86	Flory, P. J. B-113 C-351,353,364 365	Gadala-Maria, F. A. B-3
Eyring, G. B-99	Fortin, E. B-303	Gagne, R. R. C-351
Fahrenbruch, A. L. B-60 C-349,353	Fortunko, C. M. C-353	Galan, L. B-29
Fairbank, W. M. B-86 C-352	Franco, D. B-331	Galle, P. C-356
Falcone, R. W. B-150 C-358	Francois, D. C-356	Garner, C. M. B-303 C-361
Falconer, J. C-359	Frank, P. C-349	Gat, A. B-14,126
Farneth, W. E. B-49 D-368		Gautier, H. R. D-368
		Gavazza, S. D. B-25 C-354 D-368

Geballe, T. H. B-14,119,122 C-347,350,354, 362,363	Grosenbaugh, M. A. B-232	Hansch, T. W. B-276
Gibbons, J. F. B-14,126	Grover, J. E. C-352	Hanson, F. V. B-45 D-368
Gibelings, J. C. B-219	Gür, M. T. B-177 D-368	Harper, J. M. E. B-122 C-354 D-368
Gibelings, M. B-331	Gussis, G. L. B-275	Harris, C. B. C-348
Giffard, R. P. B-86	Gutfreund, H. B-194	Harris, J. G. B-10
Gilman, P. S. B-219	HaferBurns, D. J. B-41 C-354	Harris, S. E. B-150 C-347,355,358
Gochanour, C. R. B-99 C-353	Hahn, S. K. B-323	Harrison, W. A. B-153 C-350,354,361, 363
Godshall, N. A. B-177	Halbert, T. R. B-72 C-350	Hassan, M. B-5
Goldsmith, J. B-276	Halicioğlu, T. C-354	Hastings, J. B. B-41
Gooden, R. B-49	Hall, J. R. B-132	Haung, H. H. B-5 D-368
Goodfellow, J. B-164	Hall, M. A. B-272	Havlice, J. C-353
Goods, S. H. B-219	Hall, M. G. B-346	Hawkins, R. T. B-276
Green, W. R. B-150	Hallak, A. B. B-14,122 C-354 D-368	Haydon, G. B. B-155
Greenstein, H. B-29	Hammond, R. H. B-14,119,122 C-354	Hayes, S. E. B-72
Gregory, P. E. B-303 C-354,364 D-368	Hanna, S. S. B-132	Hayes, W. C. B-158 C-349,354,363
Groh, S. B-72		

Hayward, G. A. B-297	Honea, E. G. C-355 D-368	Hunter, J. B. C. B-25
Hellstrom, E. E. B-177	Hou, J. H. B-245	Hunter, S. H. B-41 C-356
Helms, C. R. C-355	Houng, Y.-M. B-205,254 C-360	Huseby, I. C. B-249,258 D-322
Henesian, M. A. B-69 C-355	Howard, R. E. B-14,119,122	Hwang, H. S. B-45 C-348 D-368
Herbst, R. L. B-69 C-355	Hsieh, C.-H. C-363	Hwang, J. R. B-5,245
Herman, T. B-126	Hsu, K. S. B-150 C-355	Ierley, G. R. B-122
Heropoulos, C. C-362	Hsu, L. S. B-25	Ilegems, M. C-356
Herrmann, G. B-161	Hsu, O. L. B-29 C-347,355	Ilonca, G. B-14
Hetherington, W. M. B-170 C-361	Hsu, S. E. C-356	Indovina, V. C-348
Hirth, J. P. C-364	Hu, Y. W. B-177	Inloes, D. S. B-275
Ho, C. B-177	Hudson, B. S. B-170 C-347,350,351 355,356,361, 363	Isied, S. S. C-356
Hoard, J. L. C-351	Hugg, J. W. B-132	Ito, H. B-232
Hodgson, K. O. B-164 C-349,350,351, 355,357,358, 364	Huggins, R. A. B-105,177 C-346,350,352 353,355,358 359,362,363	Jach, T. J. B-122 C-356 D-369
Holbrook, J. H. B-219 D-368	Humphries, G. M. K. B-209 C-356	Jackson, D. B-80
Hollenhorst, J. N. B-86		

Jacobs, R. E.  
B-170  
C-355,356

Jain, H. C.  
B-132

Jako, C. F.  
B-335

Jan, Z. S.  
B-14,323

Janousek, B. K.  
B-49

Jayarajan, A.  
B-5,245

Jenkins, M. K.  
B-84

Jew, K. G.  
B-254

Jipson, V. B.  
B-272

Johannessen, J. S.  
B-303  
C-356

Johnson, A. M.  
C-355,356,362

Johnson, F. Q.  
B-323

Johnson, K. H.  
C-353

Johnson, S. W.  
B-198

Joly, R.  
B-181  
D-369

Jones, E.  
B-205

Jones, E. D.  
B-323

Kaminsky, M. E.  
B-276  
D-369

Karp, H. A.  
B-170  
C-355

Kayali, E. S.  
B-288  
D-369

Keefer, K. D.  
B-53

Keith, D. L.  
B-14

Kerdegar, A.  
B-274

Khammouma, S.  
C-348,352

Khazzoom, J. D.  
B-5  
C-358

Khuri-Yakub, P. T.  
B-181  
C-356  
D-369

Kim, J. S.  
B-254

Kim, S.  
B-119,122

Kimhi, D. B.  
B-122

King, C. N.  
B-14,119,122

Kino, G. S.  
B-181  
C-352,353,356,  
357

Kinsman, K. R.  
C-346

Klauminzer, G. K.  
C-350

Kleeman, W.  
C-357  
D-369

Klemm, R. A.  
B-80  
C-357

Kline, M.  
C-351

Klundt, R. H.  
B-288

Knyazev, I.  
B-276

Koch, R.  
C-357

Koester, J. K.  
B-84

Komine, H.  
B-69  
C-357

Koperski, J. A.  
C-351

Kowalski, F. V.  
B-276

Krautler, B.  
C-357

Krerczien, H. J.  
B-331

Kronick, M. N.  
C-357

Kruger, C. H.  
B-84



Krumhansl, J. L. B-77	Lazarus, S. M. B-132	Lim, N. C-351
Kuehn, C. C-357	Lee, E. H. B-186	Lim, W. Y. B-5 C-358
Kugel, R. W. C-357	Lee, J. B. C-350	Lin, A. L. C-358
Kruger, E. L. B-45	Lee, S. A. B-276 D-369	Lin, J. H. B-288
Kump, M. R. B-303	Leiser, D. B. B-29	Lin, S. F. C-358,366
Kung, A. H. C-355	Leiss, J. E. B-177	Lind, J. E., Jr. B-190
Kung, J. B-331	Lemons, R. A. C-348,358	Lindau, I. B-303 C-352,358,361, 366
Kury, P. G. B-209 C-357	Leniart, D. B-29	Ling, D. T. B-303
Kutzler, F. B-164 C-351	Leung, W. P. B-282 C-353,358	Lipa, J. A. B-86
Kuznetsov, B. B-72	Levatter, G. B-69	Lips, H. I. B-190 D-369
Ladas, S. B-45	Lewis, J. T. B-209	Little, Wilbert Andrew B-132
Lam, Y.-L. B-45	Li, G. E. B-86	Little, William A. B-194 C-357,359
Lang, G. C-351	Lidow, A. B-126	Liu, S. M. B-323
Langouche, G. B-132	Lidow, D. B. B-150 C-358 D-369	Lo, T. S. B-3,288
Lao, Q.-H. B-260	Liebert, B. E. B-177 C-358	Lockhart, J. M. B-86
LaRue, G. S. B-86	Lim, K. J. B-45	Lok, B. K. B-275

Lorentz, R. B-194 C-359	Mahan, J. E. B-60 C-361	McAshan, M. S. B-86
Lothe, J. C-347,359	Mahmud, Y. A. B-132	McCarty, J. G. C-360
Lu, A. B-170	Mahrer, K. D. B-236	McConica, C. L. B-45
Lu, C.-L. B-190 D-369	Majumder, K. S. D-369	McConnell, H. M. B-209 C-348,360,365
Lublin, D. M. B-80	Mallett, R. L. B-186	McConnell, W. H. B-25 C-356,357 D-369
Luna, E. J. B-209	Malmivuo, J. B-86	McHale, A. B-29
Lund, R. W. B-219 C-359 D-369	Mark, J. E. B-113	McKenzie, J. W. B-60
Luth, W. C. B-5,196	Marrocco, M. B-72	McNelllev, T. R. C-352,356
Lyneis, C. M. B-86	Marston, P. L. B-86	Mein, J. B-10
Ma. Y. B-60	Mason, D. M. B-203 C-359	Meindl, J. D. B-215 C-361
Madey, J. M. B-86 C-352	Matlock, D. K. C-359	Meserve, R. A. D-369
Madix, R. J. B-198 C-355,359,360	Matlock, P. L. B-72	Michal, G. M. B-14,263
Madonik, A. B-72	Mattes, B. L. B-60,205,254, 323,359,360, 365	Michelson, P. F. B-86
Maeda, J. C-364	Mavis, D. G. B-132	Miller, A. K. B-288 C-360
Magnusson, R. H. B-359	Mavko, G. M. B-230 C-360	Miller, J. N, B-303
	McAllister, L. J. B-241	Miller, L. P. B-260

Mills, B. A. B-53 C-358	Murtiff, M. L. B-45	Nord, G. B-331
Minamisono, T. B-132	Mutter, M. B-113	Nordmann, R. C-357
Misemer, D. K. B-80	Mylroie, S. W. B-126 D-370	Norton, R. H. B-14,119,122
Mitchell, K. W. B-60 C-352	Nagel, D. A. B-158	Novotny, M. B-194
Mitchell, M. J. D-369	Nagel, L. E. B-335 C-346	Nur, A. M. B-228,230,232, 236 C-368,363
Miyazaki, J. B-263 C-360 D-370	Naney, M. T. B-196	Nystrom, G. B-186 D-370
Modlin, D. N. B-335	Napper, D. B-113	O'Connor, M. C. B-122
Moore, D. F. B-14,38,119 C-360	Narasimhan, S. C-347	O'Leary, T. J. B-49 D-370
Moosman, S. B-3	Neidlinger, H. B-113	Olmstead, W. N. B-49
Mortenson, L. E. C-351	Nelson, R. M. B-84	Olsen, E. M. B-25
Mortyn, F. C-347	Neuberg, K. B-72	Olson, S. T. B-158
Mottl, M. J. B-77	Neuhauser, B. J. B-86	Omelianovski, E. C-358
Mruzik, M. R. B-263 C-346,360 D-370	New, G. H. C. B-276	Ong, B. G. C-359
Murdock, J. B-209	Newton, J. H. B-150	O'Rear, D. J. B-45
Murray, J. P. B-241	Ngan, D. Y. B-198	Orlando, T. P. B-86
	Nix, W. D. B-219 C-349,352,359 360,364	

Page, B. M. C-356	Pettibone, D. B-10	Pound, G. M. B-14,263 C-346,354,358, 360,364
Paik, H. J. B-86	Pfaltz, A. C-357	Powell, R. A. B-303 C-361
Pancharatnam, S. C-359	Pharr, G. M. B-219	Preis, M. K. C-348
Panov, G. I. B-45	Phillips, J. C. B-164 C-355,361	Price, L. B-77
Pantelides, S. T. C-361	Phillips, W. A. C-347	Protopapas, P. C-361,362
Pantell, R. H. B-238 C-361	Philo, J. S. B-86	Pyzyna, M. K. B-155
Park, C.-J. C-361	Pianetta, P. B-303 C-358,361,366	Quate, C. F. B-272 C-346,348,358
Park, H. B-238	Piestrup, M. A. B-238 C-361	Radtke, A. S. B-77 C-362
Park, Y. B-238	Pietras, E. C-365	Railey, R. M. B-271 D-370
Parks, G. A. B-241 C-361	Pizzo, P. P. P. D-370	Raistrick, I. D. B-177 C-346,362
Parlee, N. A. D. B-5 C-346,354,361, 362	Plummer, J. D. B-215 C-361	Ramberg, I. C-362
Pavlath, G. A. B-282	Pocha, M. D. B-215 D-370	Reches, Z. C-362
Pearson, G. L. B-205,254 C-349,356,360	Poe, G. G. C-361	Reed, C. A. C-351
Pecora, R. B-260 C-346,347	Poppa, H. C-358	Reed, K. J. B-49 C-362 D-370
Peterson, J. A. B-77	Post, D. E. C-361	

Renner, J. L. B-77	Rose, F. M. B-72	Sanjana, V. M. B-275 D-370
Rey, P. B-209	Rosenfeld, R. N. B-49	Savcioglu, S. B-245
Rezayi, E. A. B-80	Ross, A. H. B-209 C-363	Saylor, T. K. B-132
Richards, C. W. B-274	Rothbart, G. B. B-238 C-361	Scharf, B. B-215
Richardson, J. H. C-362	Rothrock, R. K. B-72	Schawlow, A. L. B-276
Ridyard, J. N. A. C-355	Route, R. K. B-105 C-363	Schechtman, G. H. C-358
Rieder, K. B-331	Rowell, J. M. C-360,362	Schlotter, N. E. B-170
Robbins, C. B-29	Rowland, S. C. B-41 C-347,354	Schmidt, C. G. B-288
Robertson, C. R. B-275	Rusakov, A. C-350	Schmittou, E. R. B-72 C-350
Robinson, B. B-122 C-362	Rytuba, J. J. B-77	Schmuckler, G. B-72
Rodeen, H. D. B-126	Saha, S. C-363	Schneider, I. C-347
Rodgers, M. E. B-84	Saiz, E. B-113	Schoonman, J. C-363
Rodgers, T. J. D-370	Salau, A. M. B-29 C-347	Schreiber, D. E. C-346,360
Rodine, J. C-362	Salcedo, J. R. B-297	Schurman, D. J. B-158 C-349,354
Ruggiero, S. T. B-38	Salem, J. R. B-14,119,122	Schwall, R. E. C-350,363
Rønnekleiv, A. C-362,363		Schwartz, M. A. B-209

Schwettman, H. A.  
B-86  
C-352

Sears, R. A.  
B-86

Siedel, S. K.  
B-331

Self, S. A.  
B-84

Selvaduray, G. S.  
B-245

Sen, J. P.  
B-331

Seyfried, W. E., Jr.  
C-363

Shaw, H. J.  
B-282  
C-346,350,353,  
358,359,362,  
363

Shaw, I.-S.  
B-203

Sheats, J. R.  
B-209

Shen, C. C.  
B-254

Shen, Y. D.  
B-254

Sherby, O. D.  
B-288  
C-349,352,356,  
360,365

Shiah, R. T.-S.  
C-363

Shih, C. J.  
B-288

Shyne, J. C.  
C-356

Siegman, A. E.  
B-297

Silverman, D. C.  
B-45  
D-370

Simoni, R. D.  
C-363

Sklar, L.  
B-170  
C-363

Slater, J. G.  
B-25

Sliwa, J. W.  
B-219

Smith, D.  
B-126

Smith, T. I.  
B-86  
C-352

Sokel, R. J.  
B-153  
C-363

Sorrell, T. N.  
B-72  
C-351

Souquet, J.  
B-181,282  
C-362,363

Sparks, S.  
C-347

Spartalian, K.  
C-351

Spencer, J. W.  
C-363

Spicer,, W. E.  
B-14,303  
C-350,352,354,  
355,356,358,  
361,364,366

Spingarn, J. R.  
B-219

Sprunt, E. E.  
B-228

Sree Harsha, K. S.  
B-5

Stang, R. G.  
C-364

Stanley, J. H.  
B-132

Stanton, S. G.  
B-170

Stappaerts, E. A.  
B-150  
C-364  
D-370

Stark, R. A.  
B-72  
D-370

Stefan, P. M.  
B-303

Stein, C. A.  
B-331  
C-364

Stephenson, L. M.  
C-362

Stevenson, D. A.  
B-14,205,323

Stewart, G. R.  
B-122  
D-370

Strausser, Y. E.  
C-356

Sukegawa, T. C-350,364	Taylor, M. P. B-53	Tuan, H. C. B-181
Sunada, H. B-288	Teets, R. E. B-276	Turkevich, L. A. B-80
Sunami, H. C-354	Tekneci, Z. B-245	Turneure, J. P. B-86
Sundarajan, P. R. C-365	Thomas, D. D. B-209 D-371	van der Bosch, J. B-209 C-365
Surek, T. C-364	Thomas, M. E. B-263	Vander Plas, H. A. B-60 C-361
Suslick, K. B-72 C-350	Thomas, R. A. B-14,119,122	van Dover, R. B. B-38
Suter, L. J. C-364,365 D-370	Tiller, W. A. B-335 C-350,364,365	Van Kann, F. B-86
Suter, U. W. B-113	Toda, K. C-353	Vasudev, K. P. B-60,205 C-350,365
Sutton, J. B-331	Tom, G. M. C-352,364 D-371	Velez, A. B-117
Suzsco, A. M. C-359	Topsøe, H. C-348,352,365	Vetter, A. M., Jr. B-86
Swenson, L. W. C-354	Tovrog, B. S. B-72	Vine, J. D. B-77
Taber, M. A. B-86	Tremain, R. E. B-126 D-371	von Kameke, A. B-331
Tanner, F. B-117 C-356,357	Triplett, B. B. B-132	Wachs, I. E. B-198
Taube, H. B-331 C-352,359,364, 365	Trudell, J. R. C-351	Wadsworth, J. B-288
Taylor, C. M. C-362	Tsai, N. H. B-14,263	Waleh, A. B-170
	Tsang, C. H. B-342 C-365	Walker, D. B-331

Walker, R. B-72	White, G. O. B-342	Wolfe, D. C. B-69
Wallenstein, R. B-276	White, J. C. B-150	Wong, C. P. B-331
Walters, A. B. C-348	White, R. A. B-288	Worden, P. W., Jr. B-86 D-371
Wang, S. C. B-230	White, R. L. B-342,365	Wright, M. D. B-150
Warshaw, S. B-69	White, R. M. C-350,365	Wright, T. M. B-158
Waters, C. A. B-86	Wieman, C. E. B-276	Wu, F. C. B-126
Watkins, R. W. B-3,275	Wieting, R. D. B-99	Wu, M. C. B-29
Waugh, T. M. B-181 C-353,357	Wikswow, J. P., Jr. B-86 D-371	Yamada, M. B-203
Weber, R. S. B-14	Willis, M. A. B-331	Yamada, R. T. C-348
Weeks, J. D. B-232	Wilson, C. R. C-365	Yeh, C. B-254
Wei, C. J. B-219	Wilson, E. G. B-86 D-371	Yen, B. P. J. B-25
Weissbluth, M. B-340	Winick, H. C-352	Yen, W. M. B-276
Wen, J. C. B-203	Winslow, D. K. B-282 C-346,353,358	Yevitz, M. M. C-349,361
Weppner, W. B-177	Witteborn, F. C. B-86	Ying, D. B-198
Wertheimer, T. B. B-186	Wlodawer, A. B-164 C-355,361	Yoon, D. Y. C-365
Weschler, C. C-364	Wolber, P. K. B-170	Yoshida, S. B-14,45
Whitcher, B. B-99		Young, C. M. C-365



Young, E. M.  
B-335

Zych, L. J.  
B-150  
C-355

Young, J. F.  
B-150  
C-347,355,358

Young, R. W.  
B-186  
D-371

Younge, R. G.  
B-122

Youngren, G. K.  
B-3  
C-365  
D-371

Yu, K. K. Y.  
B-303  
C-355,358,366  
D-371

Yuen, C. H. C.  
B-340

Zdasiuk, G. A.  
B-150

Zercher, C. R.  
B-155

Zimmerman, A. H.  
B-49  
C-362

Zitelli, L. T.  
B-282  
C-346,353,358

Zorabedian, P.  
B-297

Zubeck, I. V.  
B-105  
C-353

Zubeck, R. B.  
B-14,119,122  
C-354